Summary of published papers by SAE, The Engineering Society for Advancing Mobility Land Sea Air and Space International. These papers discuss and review all aspects of Fischer-Tropsch diesel and natural gas-toliquid fuels.

- Bennethum, James E. and Richard E. Winsor, "Toward Improved Diesel Fuel," SAE Technical Paper Series, International Fuels and Lubricants Meeting and Exposition, Canada, 1991.
 - The paper presents the results of the Detroit Diesel Corp. test of the Rentech Fischer-Tropsch diesel fuel and discusses the significant emission reduction from the fuel and the surprising reductions from the natural occurring oxygenates that are in the Rentech Fischer-Tropsch diesel fuel.
- 2. Norton, Paul, et al., "Emissions from Trucks using Fischer-Tropsch Diesel Fuel," SAE Technical Paper Series, International Fall Fuels and Lubricants Meeting and Exposition, California, 1998.
 SAE with Department of Energy and West Virginia University tested Fischer-Tropsch diesel and blends of Fischer-Tropsch diesel on heavy trucks and buses comparing the emissions with California diesel. The results showed significant (>27%) overall reduction in pollutants with no engine modifications or fuel system modifications. In addition, blends of the Fischer-Tropsch with poorer quality California diesel produced significant reductions in pollutants and no

adverse effects in blending or vehicle performance.

- 3. Atkinson, Christopher M., et al., "In-Cylinder Combustion Pressure Characteristics of Fischer-Tropsch and Conventional Diesel Fuels in a Heavy Duty CI Engine," SAE Technical Paper Series, International Spring Fuels & Lubricants Meeting and Exposition, Michigan, 1999.

 West Virginia University (in an SAE paper) looked at the combustion characteristics of Fischer-Tropsch diesel in unmodified diesel engines. The Fischer-Tropsch diesel was found to burn at lower temperatures, with shorter ignition delays and longer combustion duration. This results in lower emissions and points to even greater emissions reduction potential in engines with fuel injection systems that are tuned for Fischer-Tropsch diesel.
- 4. Norton, Paul, et al., "Emissions from Buses with DDC 6V92 Engines Using Synthetic Diesel Fuel," SAE Technical Paper Series, International Spring Fuels & Lubricants Meeting and Exposition, Michigan, 1999.
 - The National Renewable Energy Laboratory (NREL), West Virginia University and the Department of Energy (in an SAE paper) presented a study of buses using Fischer-Tropsch diesel fuel. The conclusions are that Fischer-Tropsch diesel reduced all pollutants and provides a viable fuel in older buses needing little retrofit to improve emissions. The bus operators found no performance difference in the bus operations and less than 3% variation in fuel consumption, which is less than experienced in variations of driver technique.

5. Suppes, G. J., et al., "Type Performance of Fischer-Tropsch Liquids (FTL) in Modified Off-Highway Diesel Engine Test Cycle," SAE Technical Paper Series, International Spring Fuels & Lubricants Meeting and Exposition, Michigan, 1999.

The University of Kansas performed a study presented to SAE on the use of Fischer-Tropsch diesel and Fischer-Tropsch Liquids in Off-Highway Diesel Engines. The results demonstrated significant emission improvements and no engine performance degradation. Use of the Fischer-Tropsch liquids could lower the costs of production through the elimination of the distillation step. The crude Fischer-Tropsch performed well in the engines and reduced pollution.

Toward Improved Diesel Fuel

James E. Bennethum and Richard E. Winsor Detroit Diesel Corp.



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Toward Improved Diesel Fuel

James E. Bennethum and Richard E. Winsor Detroit Diesel Corp.

ABSTRACT

Engine hardware modifications, fuel and lube oil properties, electronic controls, and aftertreatment devices may all play a role in meeting future heavy-duty diesel engine emission standards. Detroit Diesel Corporation (DDC) is actively involved in evaluating the contributions of these technologies to reduce emissions as well as evaluating the impact on initial and life cycle system cost, fuel consumption, reliability and durability. This paper focuses on the potential of low emission diesel fuels to contribute to lower engine-out emissions.

DDC has been testing low emission diesel fuels with low sulfur and aromatics and higher cetane number, synthetic diesel fuels, and today's fuels with various additives. Other industry programs have generated similar data. These results have led us to the conclusion that a significant contribution can be made by tailoring future diesel fuels to produce low emissions. While more work needs to be done to identify what a low emission diesel fuel specification should be, this paper is intended to stimulate more interest in this subject and encourage engine manufacturers and fuel suppliers to work together to define an acceptable future fuel.

INTRODUCTION

The Clean Air Act Amendments of 1990 have established tough emission standards for heavy-duty diesel engines. The emission standards and the dates they became effective are shown in Figure 1. In the past, the burden of meeting lower emission standards has been left to the engine manufacturer. This has resulted in the development of engine systems capable of producing lower engine-out emissions. It has also spawned relationships

CLEAN AIR ACT AMENDMENTS OF 1990 U.S. HEAVY DUTY TRUCK ENGINE EMISSION STANDARDS - GM/BHP-HR

	<u>1990</u>	<u>1991</u>	<u>1994</u>	<u>1998</u>
HC	1.3	1.3	1.3	1.3
co ·	15.5	15.5	15.5	15.5
NOx	6.0	5.0	5.0	4.0
PARTICULATE	0.6	0.25	0.10	0.10

Figure 1. Heavy Duty Diesel Engine Emission Standards

between engine manufacturers and exhaust system suppliers to develop aftertreatment devices to further reduce exhaust emissions. These efforts made it clear that diesel fuel modification would be beneficial in reducing engine-out emissions and avoiding the possibility of increased particulate generation when using catalytic aftertreatment devices. The fuel modification required was reduced sulfur content. Through negotiations between the Engine Manufacturers Association (EMA) and the American Petroleum Institute (API), it was agreed that sulfur content could be reduced, and EPA specified that the certification fuels for 1991 and 1994 were to contain 0.10% and 0.05% sulfur, respectively.

The 1998 emission standards offer the most difficult challenge to date. In reducing NOx to the 4 g/bhp-hr level, particulates can be expected to increase. Further diesel fuel modifications by 1998 have the potential to offset this particulate increase. It is the purpose of this paper to review DDC's experience with various fuels and fuel additives to show that a low emissions diesel fuel (LDEF) does provide potential for significant

engine-out emissions reduction. While the idea of a low emission diesel fuel is not new (1) (2), this paper provides additional information on the potential emission reductions from use of LDEF. However, no attempt is made to provide a specification for LDEF because much more study of fuel properties and fuel cost issues is needed. It is important that engine manufacturers and fuel suppliers work together in defining a diesel fuel specification that produces lower emissions while yielding a viable product.

ENGINE MODIFICATIONS

Considerable effort is going into the development of premium heavy-duty diesel engines that can meet the 1994 emission standards without aftertreatment. The advantages of this solution are obvious in terms of system cost, installation requirements, and reliability/durability implications. Figure 2 shows the status of the S60 emission development effort as of November 1990. The engine was

1994 PROTOTYPE CONFIGURATIONS VERY HIGH INJECTION PRESSURE

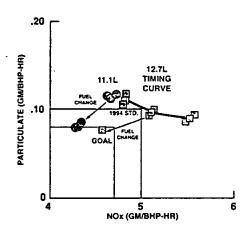


Figure 2. Effect of Low Emission Diesel Fuel on Experimental S60 Engines

close to meeting the standard using certification fuel. At that time a "reformulated" diesel fuel was tested in the engine with no further modifications. As Figure 2 also shows, by using this fuel the engine met the 1994 standards. This is significant since this change in fuel would avoid the added complexity of an aftertreatment device if further engine improvements could not reduce emissions. In the past, these observed reductions in NOx and particulate matter (PM) would have been considered "small". However, at the very low emission levels required for 1994, they represent a significant reduction in engine-out emissions.

In the case of the \$560 engine, further modifications did reduce emissions. By February 1991, a development engine was demonstrated to meet the 1994 standard with

0.10% sulfur DF-2 fuel, although it was slightly above the development goals as shown in Figure 3. However, this was accomplished by careful selection of critical components with uncertain durability. Using today's production

1994 PROTOTYPE CONFIGURATIONS VERY HIGH INJECTION PRESSURE

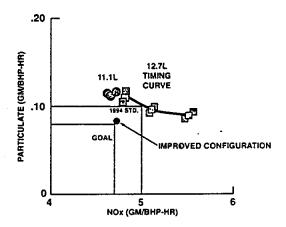


Figure 3. Addition of Further S60 Engine Improvements

technology, engine-to-engine variability and component deterioration would cause the emission standards to be exceeded during the useful life of the engine. The process of obtaining the technology to produce durable and consistent low emission components has started, but it is obvious that this will not be an easy task. Any emissions reduction that can be accomplished by fuel modifications will reduce engine manufacturing concerns and permit lower exhaust emission levels in the future.

REFORMULATED DIESEL FUELS

Diesel fuel is the result of refining crude oil to meet given specifications. Reformulated fuel can be the result of refining to a new specification or selecting materials to meet new specifications. These reformulated products have been given many other names such as clean diesel, premium diesel, high purity fuel, or low emission diesel fuel (LEDF). Some of these products are currently available in Tables I to IV represent the market place. information on products. published some Generally, the reformulated fuel has lower sulfur, a lower boiling range, higher cetane number, and lower aromatics, among other these four Reviewing differences. it is obvious that they are descriptions, somewhat different. For reference, Table V provides 1991 EPA specifications for diesel fuel used for engine emission certification.

Table VI compares the emission results with two of these fuels to emissions with 1991 certification fuel on a Series 60 emission





TABLE III

ALLIED LOW EMISSIONS FUEL

SYNTHETIC DIESEL FUEL

Specifications

PROPERTIES .	TYPICAL VALUES
Distillation, OF	
(ASTM D 86)	
IBP	370
10%	390
20%	400
50%	420
90%	475
95%	480
EP	510
Aromatics, wt	12
Flash Point, F (PM)	154
Color, Saybolt	+ 30
API Gravity @ 60°F	42
Bromine Number	0.10
Sulfur, ppm	less than 1
Nitrogen, ppm	less than 1
Carbonyl as C-O ppm	less than 10
Aniline Point, oF	less than 145
Viscosity, cSt	
70	2.17
_ 100	1.63
Frieze Point, or	less than -112
Cetane Number	53
Heat of Combustion, Btu/lb	18,585

TABLE II

GARRETT OIL/PETROCHEMICALS PREMIUM DIESEL TYPICAL SPECIFICATION

.== .	
API Gravity	43
Flash Point, min OF	150
Sulfur, ppm	<1
Color, Saybolt	+30
Pour Point, OF	<-60
Nitrogen, ppm	1
Paraffins + Naphthenes, wt%	98
Olefins, wt%	<1
Aromatics, wt%	<1
Viscosity, SUS, 100°F, sec.	32
Cetane Number	45
ASTM Distillation, OF	

IBP	365
10%	400
50%	420
90%	450
EP	550

ASTM Distillation, OF	
IBP 90% EP	332 514 555
Cetane Index	62
Sulfur Content, wt%	<.001
Cloud Point, °F	-2
Pour Point, ^o F	-6
Conradson Carbon on 10% Residuum, wt%	.05
Flash Point, °F	146
Bottom Sediment & Water, vol. %	<.025
Kinematic Viscosity @ 100°F, cSt	189
API Gravity @ 60°F	48.5
Aromatics, wt %	0
Paraffins, wt %	47
Olefins, wt %	41
Alcohols, wt %	6
Other Oxygenates, wt %	6
Heat of Combustion, Btu/1b	18,585
Heat of Combustion, Btu/gal	128,230

development engine at the 320 BHP @ 1800 rpm rating. The emissions tests conducted were three consecutive hot transient cycles on each fuel, and the average values and standard deviations of these tests is presented. Both fuels gave a NOx and PM reduction when compared to the 1991 certification fuel as shown in Figure 2.

These emission results show trends similar to those obtained by the CRC VE-1 study (3). In this work three engines were emission tested on nine fuels, and this was followed by emission tests using thirteen fuel blends on a prototype low emission Series 60 engine. Several references (4) (5) discuss the CRC VE-1 results in detail and the reader is encouraged to explore this material. Similar tests have been run in Europe and are reviewed in reference (6). These studies included eight fuels in seven different direct injection diesel engines.

FACT SHEET REFORMULATED CHEVRON SPECIAL DIESEL

DESCRIPTION:

A low-sulfur, No. 2 grade diesel fuel reformulated to reduce exhaust emissions and enhance certain aspects of vehicle performance. Expected to meet all EPA 1993 fuel requirements. Key characteristics include:

- o Minimum cetane number of 52.
- o Maximum average fuel sulfur of 350 ppm.
- o Maximum average aromatics of 30 percent.

BENEFITS:

Reduces exhaust emissions. High cetane number improves engine combustion and reduces the following emissions:

- o Hydrocarbons: Up to 40 percent.
- Carbon Monoxide: Up to 20 percent.
- o Particulate Matter: Up to 9 percent.
- o Nitrogen Oxides: Up to 2 percent.

Enhances engine performance. Improved engine combustion also results in:

- o Easier starting.
- o Smoother running.
- o Less noise.
- o Less "white smoke" during start-up.

AVAILABILITY: Introduced June 12, 1990, in the greater Los Angeles metropolitan area (Los Angeles, Orange, San Bernardino, Riverside and Ventura counties).

> Produced at Chevron's El Segundo, California refinery.

Both these fuel studies show that engine technology alters the influence of fuel parameters on engine-out emissions. Although there continues to be discussion about the results, there can be no argument that a new fuel specification could reduce emissions. The real question is "what specification will contribute the most toward reduced emissions and yet result in a commercially viable fuel?"

EPA SPECIFICATIONS for 1991 DIESEL CERTIFICATION FUELS

Property	#1 Diesel	#2 Diesel
API Gravity	40-44	32-37
Flash Point, min °F	120	130
Viscosity, cs	1.6-2.0	2.2-3.4
Sulfur, %	.0812	.0812
Cetane Number	48-54	42-50
Aromatics, min. %	8	27
ASTM Dist., OF		
IBP	330-390	340-400
10%	370-430	400-460
50%	410-480	470-540
90%	460-520	560-630
EP	500-560	610-690

TABLE VI

11.1 LITER SERIES 60 EMISSION DATA 1994 EXPERIMENTAL CONFIGURATION

(g/bhp-hr)

	<u>HC</u>	_co_	NOx_	BSP
BASELINE DF-2 (0.1% S) std. dev.				0.115 .002
GARRETT FUEL std. dev.				0.083
ALLIED FUEL std. dev.				0.085

Because of the current interest exhibited by transit authorities toward reducing urban air pollution, the Garrett and Allied fuels were also evaluated in a DDC 6V-92TA coach engine. On each fuel the emissions tests consisted of three hot transient cycles resulting in the average values shown in Table VII. These results indicate a 1% to 5% reduction in NOx and an 11% to 14% reduction in PM. No significant change was measured for HC or CO. The baseline data reflects a 1991 coach calibration running on a DF-1 low sulfur (0.1%) fuel. Unfortunately, detailed information on this fuel is not available.

TABLE VII

6V-92TA EMISSION RESULTS USING LOW EMISSION DIESEL FUELS

(g/bhp-hr)

	<u>HC</u>	_CO_	NOx	BSP
BASELINE DF-1 std. dev.	0.67	1.42 .06	4.64	0.227
GARRETT std. dev.	0.63	1.44	4.40 .04	0.195 .007
LE 4000 std. dev.	0.63	1.37	4.56 .03	0.197 .006
LE 2000 std. dev.	0.66	1.45	4.59 .02	0.201

NOTES:

LE 4000 ALLIED FUEL WITH CETANE IMPROVER
(56 CETANE)

LE 2000 ALLIED FUEL WITH CETANE IMPROVER

(53 CETANE)

The Garrett fuel showed the most reduction in both NOx and PM. This fuel has only 1% aromatic, <2 ppm sulfur, and a cetane number of 45. The Allied fuels have 15% aromatic, <2 ppm sulfur and a cetane number of 53 and 56, respectively. This suggests that the aromatics may play a more significant role than some are willing to accept. Although these emission results require substantiation by further testing, they do indicate the impact a new fuel specification could have on engine-out emissions.

FUEL ADDITIVES

There are several fuel additives in the marketplace that claim to reduce emissions and improve engine performance. Some selected references (7) (8) (9) are included for the reader to study. We have tested a number of such additives in engines at DDC without finding any measurable improvement in either performance or emissions. We do not suggest that such additives never produce positive results. We are simply stating that in clean production engines we could find no improvement when running standard emission tests with the additives evaluated.

Two additives that we consider as candidates for LEDF are cetane improvers and oxygenated compounds. Cetane improvers are already found in diesel fuels throughout North America. The Allied fuels tested used cetane improvers to raise the cetane number of their reformulated fuels to 53 and 56. Since cetane number is already included in diesel fuel specifications and is being studied by the industry, it will not be discussed further here.

Our first involvement with oxygenates in diesel fuels resulted from testing a synthetic diesel fuel, which is produced by a process based upon Fischer-Tropsch synthesis. We were surprised at the reduction in particulates that we measured compared to a DF-1 fuel used with the same engine (Table VIII). The emissions tests conducted were three hot transient cycles resulting in the average values presented. Our fuel analysis suggested that this synthetic fuel was essentially a very low sulfur DF-1 fuel without aromatics. However, the particulate reduction was much greater than would be expected from the sulfur and aromatic reductions. On further conversation with the producer, we learned that, because of the processing, oxygenated components remained in the product and the fuel tested contained several percent oxygen. Our conclusion was that the presence of oxygenates contributed significantly to the PM reduction measured. Since then we have been working with oil and chemical companies to select viable oxygenated additives for test.

TABLE VIII

EARLY 6V-92TA EMISSION RESULTS

(g/bhp-hr)

	<u>HC</u>	_co_	NOx	BSP
#1 DIESEL FUEL std. dev.	.81 .01	1.25	4.89 .02	.326 .001
SYNTHETIC FUEL std. dev.	.69 .01	1.08	5.19 .02	. 268 . 008

There are a number of properties which are important for oxygenated fuel additives being considered for use with diesel fuel. These include volatility, solubility, toxicity, odor, seal compatibility, and cost, in addition to possible effects on the low temperature pumpability, ignition quality, and stability of the fuel/additive mixture. Chemical compounds suggested include water, alcohols, esters (especially carbonate esters), di-esters, glycols, ethers, glycol ethers, nitrates, di-nitrates, di-carbonates, etc.

We considered a wide range of materials which contained from 16 to 63% oxygen and subjected a few candidate compounds to simple solubility and short-term seal compatibility tests. Unfortunately, many of the lowest cost compounds are unattractive because of volatility and solubility problems. Diglyme (diethylene glycol dimethyl ether) was selected for initial emission testing because it appeared to be a relatively safe compound and contains 36% oxygen.

As part of the work with Allied Petro, the LE2000 was provided with 0.5% diglyme added, and this fuel (LE2500) was tested on the 6V-92TA coach engine along with the other fuels. The results are shown in Table IX, which has some data from Table VII with the diglyme results added. The addition of the diglyme appears to have slightly increased the NOx to the original baseline value. However, the PM was reduced by 6% compared to the original LE2000 value. On this two-stroke coach engine, the reformulated fuel with diglyme yielded a significant 17% reduction in PM, but no NOx improvement, compared to the baseline DF-1 fuel.

TABLE IX

6Y-92TA LEDF RESULTS - INCLUDING THE ADDITION OF A DIGLYME ADDITIVE

(g/bhp-hr)

	HC	_CO_	NOx_	BSP
BASELINE DF-1 std. dev.	0.67	1.42	4.64	0.227
LE 2000 std. dev.	0.66	1.45	4.59 .02	0.201 .001
LE 2500 std. dev.	0.70 .10	1.36 .04	4.63 .04	0.188

NOTE:

LE 2500 is LE2000 with 0.5% DIGLYME ADDED

This encouraging result led us to conduct emission tests in a Series 60 engine with 5.0% diglyme added to low sulfur (0.1%) DF-2 fuel. This fuel meets EPA specifications for 1991 certification, but detailed analysis is not available. The emission testing consisted of

two hot transient cycles with each fuel, which resulted in the average values presented in Table X. NOx showed no change, but the PM value dropped from 0.169 to 0.135 g/bhp-hr, a 20% reduction. In this test HC was unchanged and CO showed a significant reduction of 13%.

We are encouraging fuel suppliers and chemical companies to identify cost effective oxygenated compounds that could be used in future LEDF formulations. Also, tests need to be conducted to determine if other properties of these compounds besides oxygen content are important to the emission reduction.

TABLE X

11.1 LITER SERIES 60 OXYGENATED ADDITIVE TEST

(g/bhp-hr)

	<u>HC</u>	<u>co</u>	NOx_	<u>BSP</u>
DF-2 0.1% S BASELINE std. dev.	0.06 .01	2.49	4.83	0.169 .008
DF-2 0.1% S with 5% DIGLYME std. dev.	0.06	2.16	4.83	0.135 .006

OTHER FUEL PROPERTIES

The discussion above has referred to sulfur content, cetane number, aromatic level, and oxygen content. Research has shown that these diesel fuel properties can have a significant effect on exhaust emissions. Nevertheless, there may be other fuel properties that should be specified in order to reduce diesel engine exhaust emissions in a cost effective manner. Some properties suggested for study include viscosity, surface tension, end point temperature, and polyaromatic content. The diesel engine and fuel industries need to support further exploration of diesel fuel properties so that a cost effective fuel specification can be derived for low emission diesel fuel.

SUMMARY

The results of engine-fuel studies indicate that a LEDF can make a contribution to reduced PM and possibly NOx and CO. The contribution of sulfur to PM is fairly well understood, but the ultimate level specified for future commercial fuels, possibly below 0.05%, will depend largely on economics. The

specific contribution of aromatics, cetane number, and other fuel properties need to be investigated further. Cetane improver additives are already used and higher concentrations should be considered to improve future LEDFs. Oxygenates, and other additives, require more effort to clarify their contribution to reduced emissions and to identify cost effective compounds that would be acceptable in commercial fuels.

Emission effects that were not considered significant when higher emission standards were being met are becoming very significant at the 1994 and 1998 heavy duty diesel engine emission levels. There is every indication that fuel changes can provide the extra margin necessary for more engines to meet these levels without aftertreatment or very expensive engine modifications. To accomplish this will require a major cooperative effort between engine manufacturers and fuel suppliers to develop a diesel fuel specification and a plan that provides improved diesel fuels to the market.

CONCLUSIONS

- Reformulated fuels, including cetane improver additives, reduce NOx and PM emissions from heavy duty diesel engines.
- Oxygenated fuel supplements can reduce particulate emissions from heavy duty diesel engines by 20%.
- A new low emission diesel fuel specification could make a significant contribution to reduced diesel engine emissions without expensive hardware.
- Further research on diesel fuel properties needs to be conducted to derive a cost effective fuel specification.

ACKNOWLEDGEMENTS

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Emissions from Trucks using Fischer-Tropsch Diesel Fuel

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Emissions from Trucks using Fischer-Tropsch Diesel Fuel

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ABSTRACT

The Fischer-Tropsch (F-T) catalytic conversion process can be used to synthesize diesel fuels from a variety of feedstocks, including coal, natural gas and biomass. Synthetic diesel fuels can have very low sulfur and aromatic content, and excellent autoignition characteristics. Moreover, Fischer-Tropsch diesel fuels may also be economically competitive with California diesel fuel if produced in large volumes.

An overview of Fischer-Tropsch diesel fuel production and engine emissions testing is presented. Previous engine laboratory tests indicate that F-T diesel is a promising alternative fuel because it can be used in unmodified diesel engines, and substantial exhaust emissions reductions can be realized.

The authors have performed preliminary tests to assess the real-world performance of F-T diesel fuels in heavy-duty trucks. Seven White-GMC Class 8 trucks equipped with Caterpillar 10.3 liter engines were tested using F-T diesel fuel. Vehicle emissions tests were performed using West Virginia University's unique transportable chassis dynamometer.

The trucks were found to perform adequately on neat F-T diesel fuel. Compared to a California diesel fuel baseline, neat F-T diesel fuel emitted about 12% lower oxides of nitrogen (NOx) and 24% lower particulate matter over a five-mile driving cycle.

INTRODUCTION

The Energy Policy Act of 1992 (EPACT) was enacted to stimulate the research, development, and accelerated introduction of alternative fuel technologies in the United States. The objective of EPACT is to reduce the nation's dependence on imported petroleum by pursuing renewable and domestically produced energy resources. Under EPACT, DOE has established programs to

promote energy diversity and the displacement of crude oil-based motor fuels.

"Gas-to-liquids" (GTL) process technology is one promising approach for achieving energy diversity. There has been heightened interest in GTL technology in recent years, as researchers and industrial firms are demonstrating good production economics. GTL fuel and chemical plants are emerging in developing countries. GTL pilot plants are also being developed for remote and off-shore applications to liberate remote and stranded natural gas reserves.

Fischer-Tropsch (F-T) is a GTL chemical conversion process that is being successfully used to produce high quality gasoline and diesel fuel products from coal, natural gas and biomass feedstocks. The process originates from Franz Fischer and Hans Tropsch who patented the synthesis of petroleum at normal pressure using metal catalysts in 1926 [1]. German industries further developed the process to produce Fischer-Tropsch motor fuels during World War II. F-T diesel fuels are typically synthesized using a three-step procedure [2-6]:

- A synthesis gas containing mostly carbon monoxide and hydrogen is produced. Natural gas is reformed with pure oxygen or air, or coal is gasified in the presence of oxygen and steam.
- Through F-T catalysis, the synthesis gas is converted into liquid hydrocarbons. The lengths of the hydrocarbon chains are determined by catalyst selectivity and reaction conditions. The process can be tuned to yield lighter or heavier hydrocarbons.
- The resulting waxy synthetic crude is upgraded using standard hydrocracking and isomerization processes and fractionated into middle distillate fuels.

In the 1950s, the South Africans further developed F-T processes to synthesize transportation fuels and chemicals from domestic coal reserves. Sasol completed a synthetic fuels plant in 1955, and further increased synthetic fuels production capacity during the oil embargo in the 1970s. Today, F-T diesel is used as a neat transportation fuel in South Africa, and also as a blend stock for use with petroleum-derived diesel to achieve low-sulfur-content specifications. Sasol has recently developed cobalt-based catalyst and slurry phase distillate reactor technology to further improve the economics for producing F-T diesel fuel [2].

Shell has developed cobalt-based catalyst technology to synthesize middle distillates from natural gas in a commercial-scale plant in Bintulu, Malaysia [3,4]. Exxon, Texaco, Chevron, Phillips, ARCO and others are also involved in developing pilot or commercial-scale plants to produce synthetic fuels and chemicals using the F-T process.

A wide array of catalyst and reactor technologies has been developed to produce F-T fuels. Consequently, synthetic diesel fuel properties can vary substantially depending on the process technology and streams being blended. But generally, F-T diesel fuels have favorable characteristics for use in compression ignition engines. Favorable attributes include:

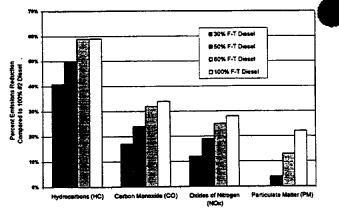
- Liquid phase at ambient conditions
- Miscible in conventional petroleum-derived diesel
- Good autoignition characteristics (cetane number of 50-75 typically)
- Low sulfur (typically less than 10 ppm)
- Low aromatics (less than 3 vol% possible)
- Energy density comparable to conventional diesel
- · Fuel tank flammability similar to conventional diesel
- Suitable for use in unmodified diesel engines
- Transportable as a liquid in existing petroleum infrastructure.

F-T diesel fuels may also be economically competitive with California diesel fuel if produced in large volumes. For a commercial-scale plant, synthetic fuel price estimates range from \$20 to \$25 per barrel of product [2,5,6,7].

The performance and emissions of F-T diesel fueled engines have been studied in engine testing laboratories [8-11]. All of these studies have confirmed that F-T diesel fuel can be used in unmodified diesel engines, and that some emissions benefits may be realized.

Sasol's Slurry Phase Distillate (SSPD) diesel fuel has been evaluated in a Detroit Diesel Series 60 12.7 liter diesel truck engine [8]. Substantial reductions of oxides of nitrogen (NO_x) and particulate matter (PM) emissions were demonstrated for SSPD and SSPD-diesel blends over the hot-start portion of the EPA Federal Test Procedure (FTP). Results for a SSPD fuel blended in conventional No. 2-D grade diesel fuel are reproduced in Figures 1 and 2. The study concluded that SSPD could

be blended with conventional No. 2-D diesel fuel in 40:60 proportions to produce emissions equivalent to a California diesel fuel.



Rigure 1: Percent emissions reduction using Sasol's Slurry Phase Distillate (SSPD) diesel fuel compared to using No. 2 diesel fuel in a DDC Series 60 engine [8].

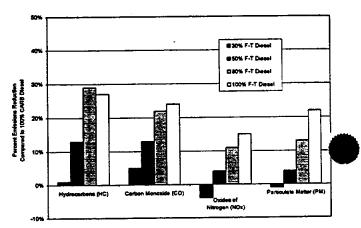


Figure 2: Percent emissions reduction using Sasol's Slurry Phase Distillate (SSPD) diesel fuel compared to using California diesel fuel in a DDC Series 60 engine [8].

Three experimental F-T diesel fuels were evaluated on an unmodified Detroit Diesel Series 60 11.1 liter diesel truck engine at Southwest Research Institute [9]. When fueled with neat F-T diesel fuels, about 3% to 8% lower torque was observed over the speed range of the engine relative to diesel-fueled torque levels. This power loss was presumably due to the lower energy density of F-T diesel fuels, and could potentially be overcome with injection timing changes. Using the same injection timing settings, brake specific NO_x and PM emissions for the neat F-T diesel fuels were on average about 8% and 30% lower, respectively, than No. 2 diesel fuel emissions for the hot-start FTP transient cycle.

Shell's middle distillate synthetic diesel fuel has recently been tested in the Daimler-Benz OM611 2.2 liter turbodiesel using a 13-mode steady-state procedure [10]. Compared to a No. 2 diesel baseline fuel, neat F-diesel fuel emitted about 6% lower NO_x and 37% lower PM on a equally weight-averaged basis. A joint European study also confirms that neat Fischer-Trospoch

fuel containing only paraffins produces similar reductions in emitted pollutants, for a variety of light and heavy duty vehicles and engines [11].

Due in part to the success of these engine laboratory tests, F-T diesel is being considered as a candidate fuel for the DOE/NREL Alternative Fuel Truck Evaluation Project [12]. F-T diesel shows promise for displacing crude oil-derived diesel fuels because of its fuel characteristics, favorable production economics, and the potential for reducing emitted pollutants. Some preliminary engine and vehicle tests were recently performed to prepare for a possible on-road demonstration of a F-T diesel fueled truck. The results of these scoping tests are reported in this paper.

TEST FUELS

Three test fuels were used for preliminary engine tests:

- No. 2-D grade diesel -EPA "on-road" diesel, 0.05% sulfur max
- California No. 2 diesel
- 100% Shell F-T diesel.

Three test fuels were used for the vehicle tests:

- California No. 2 diesel
- 50:50% F-T:California diesel blend with fuel lubricity additive
- 100% Shell F-T diesel with fuel lubricity additive.

A small batch of the F-T diesel fuel was obtained from Shell's middle distillate synthesis plant in Bintulu, Malaysia. This plant reforms natural gas with pure oxygen to produce the synthesis gas. A proprietary cobalt-based catalyst is used in a fixed bed reactor to convert the synthesis gas into liquid hydrocarbons. The waxy part of the synthesis product is selectively hydrocracked to the desired middle distillate products [3,4].

The Shell F-T diesel fuel was colorless and nearly odorless. A series of ASTM D975 diesel fuel tests and fuel lubricity rig tests was performed to determine the fuel properties, and the results are summarized in Table 1 [13]. These lab tests confirmed that the synthetic fuel met engine manufacturer specifications, and thereby ensured that engine warranties would not be invalidated while performing vehicle emissions tests. The F-T diesel fuel was found to have properties

conducive to low emissions, including a cetane number greater than 74, sulfur content less than 5 ppm, and aromatic content of about 0.3 wt%.

High frequency reciprocating rig tests (HFRR, ASTM D6079) revealed that the lubricity of neat F-T diesel fuel was unacceptable, because the wear scar exceeded the 380-micron limit specified by the engine manufacturer (Table 1). A 50:50% F-T:California diesel blended fuel was tested and also exceeded the wear scar limit, indicating that even the use of F-T blended fuels may increase wear in fuel injection system components. To prevent undue fuel system wear, the Paradyne 655 fuel lubricity additive from the Paramins Division of Exxon was added to the neat F-T fuel at a 200 ppm treat rate. The lubricity additive proved to be effective based on repeat testing on the HFRR. Lubricity tests were also performed on the SLBOCLE rig (Scuffing Load Ball-On-Cylinder Lubricity Evaluator) to further demonstrate the effectiveness of the lubricity additive for neat and blended F-T fuels.

Different variants of California No. 2 diesel fuel were used for laboratory tests, engine tests and vehicle tests. Properties of the California diesel fuel used for vehicle tests are reported in Table 1[14].

ENGINE TESTING

Preliminary engine lab tests were performed to quickly ensure that F-T diesel fuels could be used in unmodified diesel engines without significant power loss. These tests also confirmed that emissions reductions could be measured, before committing to more costly vehicle chassis dynamometer tests.

Fuel performance and emissions were compared using a 1994 Navistar T444E V8 7.3 liter diesel engine at West Virginia University. Emissions were measured for the hot-start portion of the FTP transient emissions test cycle. Triplicate emissions tests were performed for conventional No. 2-D diesel, California No. 2 diesel, and for neat Fischer-Trospch diesel fuels.

Engine performance was adequate while using neat F-T diesel fuel. Neat F-T diesel fuel emitted about 14% lower NO $_{x}$ and 13% lower PM on average, compared to the conventional No. 2-D diesel baseline fuel as shown in Table 2. The F-T diesel fuel exhibited only slightly lower emissions than the California diesel fuel based on preliminary engine laboratory testing.

able 1: Test Fuel Properties Analysis	ASTM	Units	100% F-T Diesel [13]	50:50% F-T:California Diesel [13]	100% F-T Diesel with Lubricity Additive [13]	California Diesel Fuel for Vehicle Tests [14]	Fuel Requirements from Engine Manufacturer[15]
Flash Point	D93	°C	72	101			legal limit
Cloud Point	D2500	°C	3	-5			max not above lowest ambient temperature
Water & Sediment	D1796	%	<0.02	<0.02			0.1 max
Carbon Residue	D524	wt%	0.02	0.05			1.05 max
Ash	D482	wt%	<0.001	<0.001			0.02 max
Distillation	D86	°C					
IBP			210	191		175	
10%			260	224		213	282 max
50%	1		300	282		268	
90%	1		331	332		332	360 max
FBP	, <u> </u>		338	348		363	<u> </u>
Kinematic Viscosity	D445	cSt @ 40°C	3.57	2.91	3.57		1.4 min, 20.0 max
Sulfur	D129	wt%	<0.05	<0.05			
Sulfur	D5453	ppm	<5**				3 wt% max
Sulfur	D4294	wt%				0.01	
Corrosion, 50°C for 3 hours	D130		1A	1A			no. 3 max
Cetane Number	D613		>74*	69.0			40 min
Cetane Index	D4737					53.7	
Density @ 15°C	D4052/D1298	Sp. Gravity	0.7845	0.8089		0.8337	
API Gravity @ 15.6°C	D287	°API	54	47.9			30 min, 45 max
Pour Point	D97	°C	0	-9			6° min below ambient temperature
SFC Aromatics	D5186	wt%					
Mono-			0.1	6.8			
Di-			0.1	1.1	}		
Poly-	İ		0.1	0.1			ļ
FIA	D1319	vol%					35 max
Aromatic			0.1	7.8			
Olefins		i	0.1	0.1		1	
Saturate			99.8	92.1		40.4	
Aromatics	•	mass%				18.1	10 max
Gum Content	D381	mg/l00ml	0.2	0.5	1050		3100 min
Lubricity SLBOCLE	D6078	grams	1700	3900	4050		. 1
Lubricity HFRR	D6079	micron	420/540/570	590/570	210		380 max
Carbon/Hydrogen	D5291	mass%					
Carbon			84.91	85.54			1
Hydrogen		1	14.97	14.71			1
Nitrogen	1		0.67	0.35		1	
Residual		i	-1.09	-0.595			
Oxygen (by diff)			Negligible	Negligible			
Heat of Combustion	D240	<u> </u>	100			136,400	
Gross		Btu/gal	132,600			127,900	
Net	l	l	123,600	<u> </u>		127,000	<u> </u>

^{*}Above maximum measurement capability

^{**}Below mimimum measurement capability

Table 2: Exhaust emissions from hot-start FTP engine tests in g/bhp-hr.

		47							
			No. 2 D	esel					
Test #	нс	CO NO _x		PM	CO2				
6199803	0.316	1.573	5.475	0.119	647.52				
6199804	0.352	1.578	5.367	0.121	641.86				
6199805	0.370	1.602	5.277	0.121	641.85				
Average	0.346	1.584	5.373	0.120	643.75				
California No. 2 Diesel									
Test #	HC	CO	NO _x	PM	CO ₂				
61998012	0.299	1.111	4.915	0.102	618.57				
61998013	0.293	1.136	5.049	0.106	615.06				
61998014	0.229	1.025	4.716	0.119	613.92				
Average	0.274	1.091	4.893	0.109	615.85				
	Fisch	er-Trop	sch Die	sel					
Test #	HC	CO	NO _x	PM	CO,				
6199807	0.211	0.991	4.722	0.108	610.88				
6199808	0.209	0.954	4.653	0.102	612.97				
6199809	0.174	0.959	4.445	0.101	610.62				
Average	0.198	0.968	4.607	0.104	611.49				

VEHICLE TESTING

TEST VEHICLES -The trucks used in this study were model year 1992 to 1994 White-GMC WG64T class 8 tractors (80,000 lb gross vehicle weight). The trucks were repowered with 1996 to 1997 Caterpillar 3176B diesel engines. Power System Associates (PSA) converted four of the seven trucks in the study for dual-fuel compressed natural gas/diesel operation. The dual-fuel engines are fully warranted by Caterpillar. One of the dual-fuel trucks is shown in Figure 3.



Figure 3: Pima Gro Inc. Dual-Fuel Compressed Natural Gas (CNG)/Diesel Truck

The Caterpillar 3176B is an in-line, six cylinder, 10.3 liter electronically controlled engine. Both the diesel and dual-fuel engines tested in this program were rated at 260 kW (350 horsepower). The dual-fuel engines inject natural gas into the charge air in the intake manifold and ignite the natural gas with a small charge of diesel fuel njected directly into the cylinder. By incorporating gas injectors into the intake manifold, the gas quantity is controlled for each cylinder, every cycle. Details of the

design of the Caterpillar dual-fuel engines are presented in references [16-18].

CHASSIS EMISSIONS TESTING - West Virginia University (WVU) measured emissions for this study using one of its transportable emissions laboratories. The transportable laboratory consists of a heavy-duty chassis dynamometer and an emissions measurement facility. Design details of the laboratory and previous emissions measurements using the laboratory have been presented in several previous reports [19-27].

Chassis Dynamometer — The dynamometer equipment is mounted on a fifth wheel trailer for portability. Upon arriving at the test site, the wheels of the trailer are removed and the trailer is lowered to the ground. The test vehicle is driven onto two sets of free running rollers mounted in the trailer bed. Power is transferred from the test vehicle to the dynamometer through hub adapters that are bolted to the drive wheels. The inertia weight of the truck (set to 19,000 kg for this study) is simulated by a set of flywheels. The road load is applied to the test vehicle using air-cooled eddy current power absorbers. Figure 4 shows one of the test trucks mounted on the dynamometer.



Figure 4: A diesel truck on the WVU transportable chassis dynamometer

Emissions Measurements – The emissions measurement system uses a 45.7 cm (18 in.) diameter, 6.1 m (20 ft.) long exhaust dilution tunnel mounted atop the box trailer that houses the emissions measuring equipment. Two fans and critical flow venturis control the flow rate in the dilution tunnel.

Carbon monoxide (CO), carbon dioxide (CO $_2$), oxides of nitrogen (NO $_x$), and total hydrocarbons (THC) are measured continuously throughout the test. Particulate matter (PM) is captured on a filter and weighed. Bag samples are collected and analyzed for background correction. When the vehicle being tested runs on natural gas, bags of diluted exhaust are collected and shipped to WVU for methane analysis with a gas chromatograph.

Test Method - The trucks were tested using the WVU 5-mile route. This test method is similar to the WVU

5-peak cycle reported earlier [28,29]. During the test, the truck is driven through five acceleration, cruise, and deceleration peaks. Each of the five cruise sections is at a different speed, from 32.2 km/hr (20 mph) to 64.4 km/hr (40 mph). Unlike the 5-peak cycle, which controls the rate of acceleration - thereby favoring trucks with high power-to-weight ratios - the 5-mile route allows the trucks to accelerate freely and adjusts the cruise time to keep the total distance covered constant. This allows the trucks to be driven in a manner that more closely represents on-road driving. More information on the 5-mile route can be found in reference [30]. Figure 5 shows the actual speed-time trace of a vehicle following the 5-mile route running on conventional and F-T diesel. As shown in the figure, the free acceleration rate of the truck was the same on California and F-T diesel fuel. Drivers could not detect a performance difference between trucks operating on F-T diesel and California diesel.

<u>Tests Performed</u> -The emissions tests performed are outlined in Table 3.

Table 3: Emissions Tests Performed

Engine	Fuel	Number of Tests
Cat 3176B	California Diesel	3
Diesel Engine	100% F-T Diesel	3
	50% F-T Diesel	3
Cat 3176B	California Diesel	4
Dual-Fuel Engine in Diesel-Only Mode	100% F-T Diesel	2
Cat 3176B	CA Diesel Pilot	4
Dual-Fuel Engine in Dual-Fuel Mode with Natural Gas	F-T Diesel Pilot	3
		Total = 21

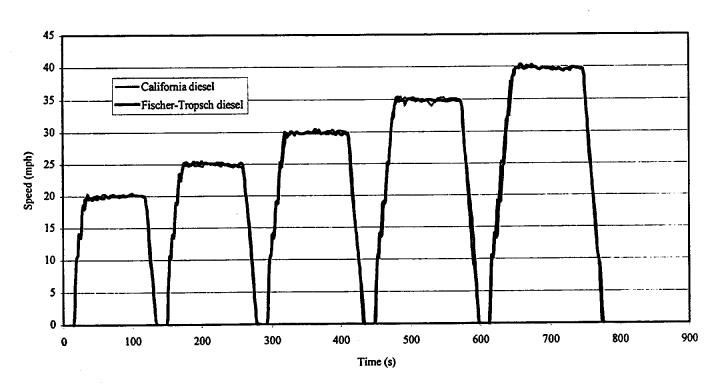


Figure 5: Speed-time trace of a test vehicle following the 5-mile route

Table 4: Average emissions (in grams per mile) and fuel mileage from tractors tested on California specification diesel, Fischer-Tropsch diesel (F-T), and a 50:50 blend of the two fuels.

				f		70.00	DICIIG	OI WILL	WU IUEIS.
Engine	Fuel	Truck Number	со	CO2	NOx	нс	РМ	MPG*	Btu/mile
Diesel Engine	California Diesel	2011	2.77	1426	14.6	0.66	0.37	6.98	18300
	California Diesel	2017	4.79	1784	13.3	0.69	0.61	5.58	22920
	California Diesel	2016	4.26	1755	12.8	0.89	0.59	5.67	22541
	50% F-T Diesel	2011	2.53	1485	11.3	0.51	0.37	6.39	19681
	50% F-T Diesel	2017	4.33	1626	13.2	0.43	0.41	5.83	21569
	50% F-T Diesel	2016	3.74	1717	11.8	0.72	0.59	5.52	22774
	100% F-T Diesel	2011	2.55	1393	11.3	0.41	0.35	6.62	18701
	100% F-T Diesel	2017**	5.37	1453	19.5	0.33	0.30	6.32	19562
	100% F-T Diesel	2016	3.21	1634	11.2	0.50	0.48	5.63	21947
Dual-Fuel Engines	California Diesel	2019	3.97	1716	12.0	0.61	0.47	5.80	22025
in Diesel-Only	California Diesel	2012	4.96	1863	14.0	0.52	0.50	5.34	23926
Mode	California Diesel	2020	3.85	1755	11.9	0.72	0.48	5.67	22526
	California Diesel	2021	5.13	1816	11.1	0.76	0.62	5.48	23323
•	100% F-T Diesel	2019	3.45	1645	10.7	0.36	0.33	5.59	22083
	100% F-T Diesel	2012	3.87	1709	13.7	0.33	0.30	5.38	22949

^{*} Miles per liquid gallon (not corrected for energy content)

Table 5: Comparison of emissions (in grams per mile) and fuel economy from dualfuel tractors tested using CNG with 100% Fischer-Tropsch diesel or California specification diesel as pilot fuels.

Pilot Fuel	Truck Number	СО	CO2	NOx	Total HC	PM	MPEG*	Btu/mile
California Diesel	2019	22.0	1444	8.17	61.8	0.43		21388
California Diesel	2012	21.3	1494	10.2	60.2	0.37	5.82	21958
California Diesel	2020	18.3	1453	10.8	47.3	0.43	6.13	20854
California Diesel	2021	17.5	1533	15.7	45.1	0.56	5.87	21769
100% F-T Diesel	2012	21.7	1528	7.59	72.6	0.35	5.15	23976
100% F-T Diesel	2020	17.8	1471	7.36	80.2	0.42	5.27	23452
100% F-T Diesel	2021	16.3	1478	12.4	62.7	0.56	4.31	28649

^{*} Miles per Equivalent Gallon – Miles per diesel equivalent gallon containing 127,900 Btu for the California diesel and 123,600 for the Fischer-Tropsch diesel.

^{**} The driver during this test reported that truck 2017 began to behave erratically during the test on F-T diesel. The behavior was not attributed to the fuel. The truck displayed a "check engine" light shortly after being returned to the fleet. Data from this truck were not included in the averages shown in Figures 6 and 7.

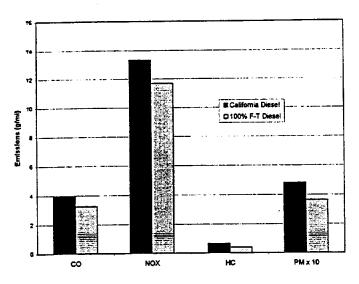


Figure 6: Average emissions from four trucks (2011, 2016, 2012, and 2019) operating on California diesel and 100% Fischer-Tropsch diesel.

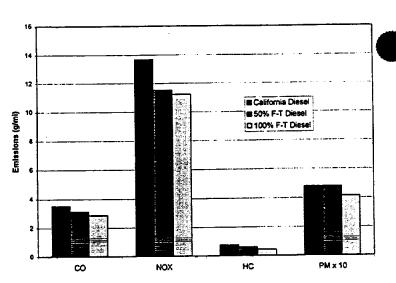


Figure 7: Average emissions from two diesel trucks (2011 and 2016) operating on California diesel, a 50% Fischer-Tropsch diesel blend and 100% Fischer-Tropsch diesel.

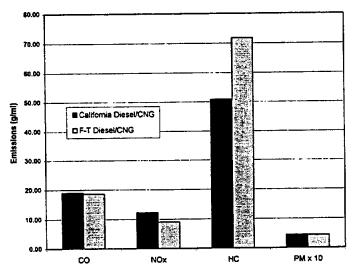


Figure 8: Average emissions from three dual-fuel trucks (2012, 2020, and 2021) operating on CNG with a California diesel and 100% Fischer-Tropsch diesel pilot charge.

RESULTS

The average emissions results are summarized in Tables 4 and 5. At least three measurements were taken and averaged for each result presented in the tables.

Five trucks were tested on California diesel and 100% F-T diesel. The average results for four of these vehicles are illustrated in Figure 6. (The results for truck 2017 were not included in the average due to erratic behavior of the truck during testing.) Use of F-T diesel in place of California diesel in these trucks led to lower levels of all four emissions measured. NO_x was reduced by an average of 12%, PM was reduced by an average of

24%, CO was reduced by an average of 18%, and THC emissions were reduced by an average of 40%.

These four trucks had essentially the same average fuel consumption on an equal energy basis when they were run on F-T diesel and Califórnia diesel. The truck-to-truck variation in fuel consuption on California diesel (about 19%) was much greater than the difference in fuel consumption for any given truck on California and F-T diesel (about 4% maximum). The lower heating value of the F-T diesel (123,600 Btu/gal) is about 3% less that the California diesel (127,900 Btu/gal); therefore, the range of a truck on F-T diesel will be slightly less than on California diesel.

Three diesel trucks were tested on California diesel, a 50% F-T and California diesel blend, and 100% F-T diesel. Figure 7 shows the average results for two of these trucks (truck 2017 was not included in the average). The 50% blend reduced the NO_x emissions com the truck nearly as much as the neat F-T diesel, but PM emissions were not reduced.

Three dual-fuel trucks were tested with compressed natural gas as the primary fuel and either California diesel or F-T diesel as the pilot fuel. The average results of these tests are shown in Figure 8. The dual-fuel trucks emitted less oxides of nitrogen and higher carbon monoxide and total hydrocarbons than than the diesel trucks on both California diesel and F-T Diesel. Using the F-T diesel as the pilot fuel in place of California diesel lowered NO_x emissions by an average of 26% and increased THC emissions by an average of 41%. CO and PM emissions were essentially unchanged.

CONCLUSIONS

- The Shell Fischer-Tropsch synthetic diesel fuel had properties conducive to low emissions, including a cetane number greater than 74, sulfur content less than 5 ppm, and aromatic content of about 0.3% by weight.
- Fischer-Tropsch fuels and blends may require a lubricity additive to prevent undue fuel injection system wear based on rig test results. A commercially available lubricity additive was found to be effective for this study.
- Drivers could not detect a performance difference between trucks operating on F-T diesel and California diesel.
- Use of Fischer-Tropsch diesel in place of California diesel in the test trucks led to lower levels of all four regulated emissions measured. Oxides of nitrogen were reduced by an average of 12%, particulate matter was reduced by an average of 24%, carbon monoxide was reduced by an average of 18%, and total hydrocarbon emissions were reduced by an average of 40% for diesel-powered test trucks. Greater emissions benefits would be realized when subsituting Fischer-Tropsch diesel for 49-state No. 2 diesel.
- Vehicle performance and emissions results were promising enough to justify a more thorough fleet evaluation in revenue service with Fischer-Tropsch diesel.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

CNG – Compressed Natural Gas CO – Carbon Monoxide

DDC - Detroit Diesel Corporation

DOE - U.S. Department of Energy

EPA - Environmental Protection Agency

EPACT - Energy Policy Act of 1992

F-T diesel – Fischer-Tropsch diesel

FTP - Federal Test Procedure

GTL - Gas-to-liquids

HC - Hydrocarbons

HFRR - High Frequency Reciprocating Rig

NO_x - Oxides of Nitrogen

NREL - National Renewable Energy Laboratory

PM - Particulate Matter

ppm - parts per million

SLBOCLE - Scuffing Load Ball On Cylinder Lubricity Evaluator

SSPD - Sasol's Slurry Phase Distillate

THC - Total Hydrocarbons

WWU - West Virginia University

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ABSTRACT

The emissions reduction benefits of Fischer-Tropsch (FT) diesel fuel have been shown in several recent published studies in both engine testing and in-use vehicle testing. FT diesel fuel shows significant advantages in reducing regulated engine emissions over conventional diesel fuel primarily to:



- its zero sulfur specification, implying reduced particulate matter (PM) emissions,
- its relatively lower aromaticity, and
- its relatively high cetane rating.

However, the actual effect of FT diesel formulation on the in-cylinder combustion characteristics of unmodified modern heavy-duty diesel engines is not well documented. As a result, a Navistar T444E (V8, 7.3 liter) engine, instrumented for in-cylinder pressure measurement, was installed on an engine dynamometer and subjected to steady-state emissions measurement using both conventional Federal low sulfur pump diesel and a natural gas-derived FT fuel. The in-cylinder combustion pressure traces obtained during the engine testing were analyzed to obtain several pressure-based variables including ignition delay, combustion duration, peak pressure, location of peak pressure, relative quantities of premix and diffusive burn heat release, indicated mean effective pressure, and location of one-half of the mass fraction burned.

These parameters were chosen because of their well-known effects on regulated gaseous and particulate matter emissions. The emission variations between the two fuels tested were compared to the differences in the measured combustion characteristics, and an explanation for the lower NOx and PM emissions of FT was developed.

INTRODUCTION

There is growing concern that a significant reformulation of diesel fuel will be required if heavy duty engines are to meet 2002 emission specifications and if light duty

diesels are to make significant inroads into the SUV market. This is particularly important now that the California Air Resources Board is seeking to harmonize light duty diesel and spark ignition vehicle emissions standards with their LEV-II standards. The diesel-fueled engine has recently been besieged with concerns over its contributions to the atmospheric emissions inventory. Diesel particulate matter (PM) has been suggested to pose health risks: specifically, the high number count of ultrafine PM particles is under scrutiny [1]. Recently, forty compounds have been identified in diesel volatile organic emissions (in the hydrocarbon emissions) and PM emissions as toxic compounds [2]. These factors, and the impending reduced emissions levels prescribed for the year 2002, will act as a driving force to improve diesel engine technology and increase the efficiency of aftertreatment devices. However, it is also possible to reduce diesel engine emissions through the use of compression fuels ignition reformulation of diesel fuels. Advanced, zero-sulfur, diesel fuels will reduce deactivation of advanced aftertreatment devices [3]. The United States (US) already has reduced the permitted sulfur content of fuels, to reduce PM, and the State of California has specified fuels with lower aromatic content for diesel engine use. This paper presents emissions and incylinder combustion pressure data from a Navistar diesel engine operating on Fischer-Tropsch (FT) fuel and 49-state diesel fuel. FT fuel is attractive because it is not necessarily derived from crude oil (in this case it derives from natural gas), and so offers future economic and strategic alternatives to US oil importation.

LITERATURE REVIEW

Recently, FT diesel fuel has received attention as a high quality, low emissions diesel substitute. FT is produced from gasification products, using either natural gas or coal as the feedstock. In the Sasol Slurry Phase Distillate Process [4] used in South Africa, synthesis gas is reformed to produce carbon monoxide and hydrogen, then converted into heavy hydrocarbons by means a Fischer-Tropsch process employing metal catalysis. These waxy hydrocarbons are then refined (using distillation and hydrocracking) to produce cuts that correspond to a range of conventional refinery products.

FT composition can vary substantially as a result of the catalysts and conditions used in the conversion, but products generally have vanishing low sulfur levels, and high cetane numbers with low aromatic content. The fuel has a high degree of saturation. Schaberg et al. [4] presented hot start transient emissions data from a Detroit Diesel Series 60 engine using 49-state diesel fuel, California diesel fuel and two South African Sasol FT fuels with different properties. The neat FT had cetane numbers of over 73. The 49-state diesel had an oxides of nitrogen (NOx) emissions level 18.2% higher than the California diesel, while the two FT fuels had NOx emissions 14.1 and 14.8% lower than the California diesel. FT PM values were 21.1 and 22.5% lower than the California diesel and HC emissions for FT were also substantially lower than for either diesel fuel. They showed that emissions of California fuel could be matched with a blend of 40% FT and 60% 49-state diesel. It was demonstrated that, unlike biodiesel, FT does not suffer from the same NOx-PM tradeoff and benefits diesel engine emissions reductions across the board.

Recently, Norton et al. [5] presented data comparing the emissions of a Malaysian FT with California diesel. Vehicles equipped with Caterpillar 3176 engines were subjected to chassis dynamometer-based emissions characterization using the West Virginia University (WVU) 5-mile route test schedule [6]. Data showed the advantage of the FT diesel in reducing both NOx and PM emissions in real-world usage.

Ultra-low-sulfur (<0.005%) diesel fuels have been introduced in Europe to reduce the PM levels from urban buses [7]. A 32 to 44% reduction in PM was obtained in buses with pre-EURO 1 engines and approximately 32% reduction in PM was obtained in buses with EURO 2 engines, while using ultra-low-sulfur European "City" diesel.

A recent report by Sirman et al. [8] detailed the results of certification diesel and six alternative diesel fuels in an unmodified, direct injection 2.2 liter Daimler-Benz OM 611 diesel engine operating at steady-state speed and load points. It was recognized that by using absolute speed-load points, a comparison of the emissions can be made based on differences in fuel consumption and chemistry, not on power variations due to fuel density variations. Data showed a reduction in PM without any significant increase in NOx. The results also showed that CO was reduced for the steady-state points for the six alternative diesel fuels relative to the certification diesel fuel.

Any comparison of emissions from regular or alternative fuels should take into account recent research on the influence of petroleum diesel fuel properties on emissions from compression ignition engines [9,10,11]. Problems arise in quantifying the emissions effects of fuel density, energy content, and viscosity because these properties can affect the ignition timing and injection mass quantity, while a lowered energy density can serve to de-rate an engine. It is important to clarify in all circumstances whether the various fuels were employed in an unaltered engine or whether timing and injection quantity were adjusted in any fashion. Mann et al. [9] have argued, for example, that a NOx increase arising from a diesel density increase is negated if fuel

delivery and actual injection timing are matched for the higher and lower density fuels.

In the present study no engine control parameters were changed: the objective was to assess the behavior of the fuel if used as a direct diesel fuel replacement. Mann et al. [9] reported data for a 2 liter Rover automobile diesel engine operating on seven different fuels. With the engine controls unaltered, PM was reduced when lower density fuels were used, whereas NOx was increased. However, this work proceeded to show that results may be attributed to interactions with the engine controls in addition to combustion behavior of the fuels. For example, kerosene, representing a light fuel, suffered an ignition delay of over 0.3 degrees of crank angle relative to a dense diesel fuel merely due to its physical properties.

There is a growing body of data demonstrating the benefit of advanced fuel formulations in reducing diesel engine emissions, but further research is still needed to relate the advantages to fuel properties.

In several other recent studies [12,13], FT has shown significant potential in reducing exhaust emissions from heavy duty diesel engines. It is acknowledged that the high cetane rating of FT fuel can reduce the premix burn fraction in diesel engines and hence reduce NOx formation during its initial combustion. It is clear that reductions in PM are due to the zero sulfur specifications of the fuel (hence eliminating the sulfate contribution to particulate matter mass), and that the high degree of fuel saturation may reduce PM although Mann et al. [9] found no statistically significant relationship between the polyaromatic content in the fuel and the production of PM. It is also true that the FT fuels, having lower mass and energy densities, de-rate an engine slightly relative to diesel, and this can serve to reduce PM.

It should be noted that, in this study, all exhaust emissions levels are reported on a brake specific energy basis, removing the effect of any small variations in power output on the measured emissions.

EXPERIMENTAL PROCEDURE

A 1994 specification Navistar T444E direct injection diesel engine was used in this study [14]. The T444E engine was a four-stroke turbocharged V8 with overhead valves and a compression ratio of 17.5:1. The engine is rated at 138 kW at 2550 rpm and 600 Nm at 1510 rpm. The engine was heavily instrumented and connected to a data acquisition system consisting of a 486 class personal computer containing a DAS-16 data acquisition board, a CTM-10 counter timer board and a DAS-58 high speed simultaneous sample and hold board. The DAS-58 was used to sample in-cylinder pressure signals generated by piezoelectric pressure transducers (PCB Piezotronics, Inc.) flush mounted in cylinders #3 and #5 of the engine as well as an index signal that provided information on top dead center of cylinder #1. The CTM-10 was used to record engine speed, fuel injection pulse width, injection timing, and manifold air pressure. The DAS-16 recorded various engine temperatures, injection control pressure, engine load, accelerator pedal position and the emissions levels. The parameters that were monitored are shown in Table 1.

FUELS USED

The two fuels used in this study were a base 49-state diesel fuel and a natural gas-derived FT fuel. It should be borne in mind that, just as in the case of so-called "diesel" fuel, the designation "Fischer-Tropsch" fuel represents a generic type of fuel, rather than a fixed fuel specification. As a result, there are potentially an infinite number of "FT" fuels that each could have their own unique fuel specification (i.e. density, cetane number, sulfur level, and aromatic content). Insofar as exhaust emissions are known to depend on these specifications, they are reported in Table 2 for the two fuels tested in this study. The FT fuel is the same as reported in a prior study [12]. The D2 fuel properties shown are typical, being from an analysis of a subsequent fuel batch from the same supplier; they are not the result of an analysis of the actual fuel used.

TEST PROCEDURE

Twelve separate nominal engine load and speed settings were chosen to span a wide range of engine performance as shown in Table 3. The data from this table shows the FT fuel suffering a general de-rating of the engine torque output at the maximum load points (2, 5, 8, 11, and 12); the maximum percent difference between the set torque and the measured torque for FT is 3.2% lower for Point 8. The intermediate load points (1, 3, 4, 6, 7, 9, and 10) for the FT fuel are within 1.4% of the D2 measured load. It should be recognized that the FT load is greater than the D2 load at Point 10. For each set point, the engine was brought to the appropriate speed and load and allowed to settle into a steady state condition in order to prevent transients in operating conditions and to provide steady and repeatable emissions production. Once all parameters of interest had achieved a steady state condition, data acquisition was initiated. Every revolution of the engine generated a trigger signal for the acquisition of the designated "slowspeed" variables such as manifold boost pressure, intake air temperature, engine coolant temperature, advance, engine speed, emissions, etc. After a set number of revolutions, a trigger initiated the "high-speed" acquisition using the DAS-58. With the pressure signals from two cylinders and the TDC phasing signal being recorded, the DAS-58 was capable of acquiring complete pressure histories for 128 successive combustion events. As a result, the data presented are averages for 640 points for the engine parameters collected by the DAS-16 board and averages of 128 cycles for the pressure derived parameters obtained by the DAS-58 board.

EMISSIONS MEASUREMENT

As described in CFR 40 [15], the exhaust gas was routed to a full-scale dilution tunnel where the exhaust gas was diluted with pre-conditioned air. The exhaust gas and dilution air were pulled by a blower through a metering venturi operating at a choked condition. The emission concentrations of THC (total hydrocarbon), CO₂, CO, NOx, and PM were measured continuously with the equipment listed in Table 4. Although the 70 mm litter method is used for certification of PM levels from

diesel engines, the R&P 1105 TEOM instrument was used to collect continuous PM data as listed in Table 4. The THC analyzer was a flame ionization detector (FID). The $\rm CO_2$ and $\rm CO$ concentrations were measured with non-dispersive infrared analyzers. The chemiluminescence method was used for the detection of NOx emissions.

The tapered element oscillating microbalance (TEOM) Model 1105 provides real-time information about the instantaneous PM. The TEOM pumps a constant flow sample of diluted exhaust gas through a small filter, the mass of which is continuously inferred [16-18]. The key component to the TEOM is a hollow, tapered, oscillating element on which the filter is mounted. During operation, the element oscillates at its natural frequency. Simply, it can be represented by a spring-mass system in which a change in mass correlates to a change in resonant frequency. As the filter weight changes due to particulate build up, the frequency of the element oscillation changes. By measuring the resonant frequency, the change in mass on the filter can be inferred. The TEOM measures the frequency of the element oscillation and calculates a change in filter weight at approximately 20 Hz.

Three outputs from the TEOM instrument can be used to infer PM. The mass rate (g/s) and mass concentration (mg/m³) are related by the flow rate through the TEOM. The total mass is the integrated value of the mass rate over time. An average mass rate as measured by the TEOM was then related to the total engine out PM flow rate value through knowledge of the dilution tunnel flow. TEOM data in transient use also detects increasing and decreasing water vapor deposition rates on the filter, but at steady state operation, this problem is obviated.

IN-CYLINDER PRESSURE SIGNAL DERIVED PARAMETERS

PCB Piezotronics, Inc. piezoelectric pressure transducers (model 145A01) were installed in cylinders 3 and 5 through the holes originally intended for the glow plugs. They were flush mounted and, once installed, the engine was motored to provide the correct phasing information for the crank position sensor. Plots of pressure versus volume for the motored cylinders allowed for more precise determination of top dead center and final analysis showed straight compression curves with no crossover and met the checks of accuracy provided by Lancaster et al. [19]. An optical encoder connected to the end of the crankshaft assembly provided a trigger for the data acquisition system at a rate of 1024 points per revolution.

The transducers did not suffer from thermal drift to any significant degree, but each combustion cycle was nevertheless pegged to the intake manifold air pressure. In order to approximate that, the first 20 points of each cycle were averaged and this value was set to the corresponding MAP value in order to calculate the actual pressure during the rest of the cycle.

Indicated mean effective pressure (IMEP) was calculated by integrating the work performed on the piston and dividing through by the displacement volume. This was done computationally by finding the difference

between the volume at each time step and the previous time step, multiplying by the applicable pressure and integrating this product over the entire power cycle. Because the exhaust cycle was omitted, the subscript "g" has been placed onto IMEP to indicate the gross amount of work done.

Ignition delay provided a measure of the time between the crank angle when the fuel was actually injected and the point at which discernible combustion occurred within the cylinder. Discernible combustion has been defined in a number of ways: from the point at which the pressure history deviates from a theoretical motoring curve to the point at which either 1% or 10% of the mass fraction has burned depending upon researcher preference [20,22]. Ignition delay in this paper has been defined as the time in crank angle degrees from injection to where pressure due to combustion deviates from a theoretical compression curve.

Combustion duration has been defined in this paper as the time between 10% and 90% of the mass fraction burned in crank angle degrees. The algorithm used for this parameter is based upon the First Law of Thermodynamics and is the same as that used for the ignition delay. In practice, the incremental heat added is summed over a range and then looped through the program again to determine the points at which 10% and 90% of combustion has occurred. Combustion in this definition includes the heat transferred to the cylinder walls as the algorithm is based on the first law analysis explained later in the paper.

Additionally, several other parameters were calculated from the pressure histories. The location of 50% mass fraction burned, or LMFB50, is calculated as the point at which 50% of the mass fraction of fuel has burned. The maximum burning rate and its location are calculated through a five-point central difference differentiation algorithm, and the maximum instantaneous torque generated and its location are monitored for each combustion cycle. The instantaneous torque value is calculated from the geometric parameters of the engine that provide a moment arm which is then multiplied by the total downward force impinging on the piston determined from the pressure recorded at that point.

Finally, the incremental heat addition calculations provide three additional parameters: the mixing burn, defined as the time in crank angle degrees for the mass fraction burned to go from 50% to 99%; the maximum heat added defined as the highest calculated incremental heat value that occurs in the cycle; and the location of the maximum heat added. These are all byproducts of the combustion duration calculations already being performed. In a typical diesel combustion process, there are two distinct burning phases that can be seen in the heat release information: the initial heat release spike (premix) and the longer oxidation time (diffusion). The mixing burn duration attempts to approximate the oxidation burning sequence. Table 5 gives a complete description of the combustion derived parameters used in this study.

The basic algorithm used in previous studies [21,22] with some success is derived from the First Law of Thermodynamics and assumes a quasi-static condition within the combustion chamber, that is that the combustion occurs at a uniform temperature and

pressure. Unfortunately, the diesel direct injection process presents problems with this assumption and consequently any method of analysis based on this can only give approximate answers. Problems with the assumption include the presence of crevice volumes that do not behave quasi-statically, the burned gas composition which is unknown, non-uniform air-fuel ratios during combustion and inaccuracies involved in the prediction of heat transfer to the walls of the cylinder [22].

The equation for the first law analysis is

$$\frac{dQ}{dt} - p\frac{dV}{dt} + \sum_{i} \dot{m}_{i} h_{i} = \frac{dU}{dt}, \qquad (1)$$

where Q is the heat transferred, p is the pressure, V is the volume, m_i is the mass of fuel injected, h is the enthalpy and U is the internal energy. Since the only mass crossing the system boundary, neglecting blowby, is the fuel injected, the mass-enthalpy term reduces to a mass of fuel enthalpy term. Assuming that the enthalpy and internal energy are sensible terms (using a baseline of 298 K) and that the net heat released is defined as the difference between the energy released through combustion and the energy lost to heat transfer from the system, the equation can be rewritten as

$$\frac{dQ_n}{dt} = p \frac{dV}{dt} + \frac{dU_s}{dt}.$$
 (2)

The heat transfer lost through the system boundary presents a problem only at the end of combustion where temperatures have risen. Studies have shown that the energy lost due to heat transfer does not affect the ignition delay parameter significantly [22,23]. The fue enthalpy difference is sufficiently small to be negligible. Next, the system is assumed to behave as an ideal gas

$$\frac{dQ_n}{dt} = p\frac{dV}{dt} + mc_v \frac{dT}{dt},$$
 (3)

where c_v is the specific heat at constant volume. Differentiation of the ideal gas law with R assumed constant provides a means of eliminating the temperature term which is generally unavailable in pressure analysis. Equation 3 can be expressed as

$$\frac{dQ_n}{dt} = \left(1 + \frac{c_v}{R}\right) p \frac{dV}{dt} + \frac{c_v}{R} V \frac{dp}{dt}.$$
 (4)

Substituting the specific heat ratio, γ , provides the final equation used in the analysis with the result being equally valid when substituting the independent variable θ , or crank angle (CA), for time, t; the resulting equation is given as

$$\frac{dQ_n}{d\theta} = \frac{\gamma}{\gamma - 1} p \frac{dV}{d\theta} + \frac{1}{\gamma - 1} V \frac{dp}{d\theta}.$$
 (5)

RESULTS AND DISCUSSIONS

Table 6 shows the normalized emissions rates of each species of interest for each fuel. These tables show that each speed and load set point displays substantial

similar emissions results on each of the two fuels, implying that while the absolute emissions levels are different for each of the two fuels, the two fuels do behave substantially similar in their emissions at any particular speed and load tested.

Figures 1 to 5 show the relative levels of emissions at each set point of the two fuels. From Figures 1 to 5, FT shows the general trend of reduced emissions (except for small differences in HC at Points 2, 4, and 5). As shown in Figure 6, the peak measured in-cylinder combustion pressure is lower for FT for all of the speed and load set points.

The lower brake specific CO₂ emissions in Figure 3 for FT fuel are reflective of the higher degree of saturation for the FT than for diesel, which contains more olefins and aromatics. It is also recognized that the FT fuel has a lower density but slightly higher energy content (net heat of combustion per unit mass).

In Figure 4, all twelve operating points show reductions of NOx emissions on FT. It is evident that FT most benefits the NOx reduction (as a percentage) under light and medium load points (1, 3, 6, 9, 10 and 12) and has less effect under full load operation points (2, 5, 8, and 11). This is because the light load conditions emphasize NOx production from premix burn, while full load points include both premix and diffusion burn contributions. Figures 7 and 8 emphasize the benefit of FT in reducing premix burn duration. Figure 5 illustrates that the majority of the speed and load set points show PM reductions of 25 to 40% between D2 and FT. The greatest PM reductions are at moderate and high loads at each speed. For example, Points 4 and 5 (moderate and high loads) show an approximate 30% reduction in the PM whereas Point 3 (low load) only shows a 15% reduction.

Figure 9 presents combustion and ignition delay information for the diesel and FT fuel. At all operating conditions, the FT yielded a shorter ignition delay than the diesel, as a result of its higher cetane rating. Ignition delay was of the order of 10 degrees of crank angle, which represents a delay of 1.1 milliseconds at 1500 RPM. The FT fuel typically enjoyed a delay period about one tenth of a millisecond less than diesel, and this was able to aid in reducing the physical evaporation occurring before ignition. As a result, the FT fuel yields a more consistent heat release rate shape, and serves in this way to reduce NOx. There was no trend of the difference in ignition delay between the two fuels being related to load.

Figure 9 also shows that the FT fuel had a slightly higher burn duration than the diesel fuel. Even when the earlier ignition was considered for the FT, the total period for delay and burn was longer than for the diesel fuel. The point in the cycle at which 50% of the fuel is burned is given in Figure 10, FT is longer for the 12 set points. The sum of the ignition delay and combustion duration for each fuel is roughly equivalent, with the variations between each fuel never differing by more than about 1.5 crank angle degrees in a total of 25 or 30. Nevertheless, the time taken to burn half of the fuel is longer in the case of the FT than the diesel. This is emphasized in Figure 11, which shows that the location of peak pressure occurs slightly later, and differs little.

Figure 6 echoes the data from Figure 11, by showing that the peak combustion pressure generated by FT is lower than the peak pressure for diesel at each speed and load set point. This is naturally explained in most cases by the fact that the piston has passed farther down the expansion stroke by the time the peak pressure is encountered. However, even in three cases, shown in Figure 11, when the F-T peak pressure occurred earlier, the peak pressure value for the FT was lower than for diesel. Figure 12 shows the maximum burn rates, expressed as a pressure rise rate, for both fuels at all twelve operating conditions. Since the data points are all close to near top dead center, the rate of pressure rise is nearly directly proportional to the actual heat release rate. In all cases the maximum FT burn rate is substantially lower than the maximum diesel burn This is because the diesel combustion has a strong premix component, whereas the FT burn is more steady over the burn duration. Consider, for example, Points 3, 4, and 5 in Figure 12. All represent an engine speed of 1500 rpm and the torques are 271, 542, and 621 Nm, respectively. The maximum diesel burn rates all lie between 6.4 to 7.6 kPa/µs for these three points, because the premix burn rate is not strongly affected by the load above a minimum fuel injection quantity. The FT maximum burn rate, however, is strongly affected by the quantity injected (varying from 3.5 to 5.4 kPa/µs), indicating that the premix burn is less influential in the combustion of the FT.

Any simple argument to explain the comparison of diesel and FT maximum burn locations in Figure 13 appears quixotic. One might expect that the maximum burn location for diesel would always be the premix burn location, and that the FT location might be somewhat later, but in four cases the F-T maximum burn location is earlier than the equivalent diesel location. In these cases it is likely that the higher cetane rating initiated significant combustion of the FT before the diesel, while in the remainder, the lack of strong premix burn for the FT would have delayed the maximum point. However, Figure 14 shows an unambiguous trend for the maximum instantaneous indicated torque during the expansion stroke: it is always slightly lower for the FT fuel, although the location may occur before or after the diesel location, as shown in Figure 15. Figure 16 demonstrates that for most of the test points, the FT takes longer to complete the second half of the fuel burn than the diesel.

The maximum heat release, deduced from the piston motion and the in-cylinder pressure behavior, includes the effect of heat transferred to the piston and walls. Figure 17 shows that trends are in sympathy with the maximum pressure rise data, shown in Figure 12. In a similar way, Figures 18 (maximum heat release location) and 13 (maximum pressure rise location) are strongly related.

Figure 19 provides a summary plot of the steady state NOx production (in g/s) as a function of power density (as indicated by gross mean, effective pressure). The diesel data and FT data are each well represented by a linear trend of NOx against indicated power, although both show an upturn in NOx at the higher power levels. The benefit of FT in yielding less NOx at similar power densities is evident by the trend lines. The diesel and FT data are collapsed into a single trend when NOx versus peak combustion pressure, Figure 20, and NOx versus

measured exhaust temperature, Figure 21, are considered. Figure 21 emphasizes that for the same exhaust gas temperature (indicative of the same average in-cylinder temperature) both FT and D2 produce the same levels of NOx. This is encouraging as it does not suggest any difference in the mechanism behind the NOx formation reaction, but merely that for the same net power output at any speed, the FT results in a lower average in-cylinder temperature. It implies further that a Zeldovich type mechanism, which suggests an exponential dependency on temperature, is an accurate model for the NOx formation reaction in both D2 and FT fueled engines. For each of the nominal speed and load set points, the FT showed a lower exhaust temperature thus resulting in lower NOx than for the D2.

Figure 22 shows that FT has a somewhat more favorable NOx-PM behavior than does D2, as is to be expected from the brake specific emissions results. Figure 23 displays the relative emissions reduction of NOx and PM for FT, compared to D2, as a function of load for the different speed set points; the relative NOx reduction for FT decreases with load while the relative PM reduction increases with load.

Figures 24 to 28 show average in-cylinder combustion pressure profiles at each of the speeds and loads for the two fuels, demonstrating the reduced ignition delay and typically longer combustion duration for FT. Although these figures illustrate that the FT pressure is generally lower around top dead center, the gross indicated work of FT is within 0.3% of the D2 indicated work, on average, for the intermediate load points (1, 3, 4, 6, 7, 9, and 10). This difference is insignificant and is attributed to the resolution of the data acquisition system. However, the maximum load points (2, 5, 8, 11, and, 12) suffer an average 2.1% reduction in the indicated work, as supported by the measured dynamometer load data in Table 3, showing the minimal derating effect of the lower density FT fuel.

It should be re-emphasized that most of the emissions levels reported here are on a brake-specific basis, removing the effect of any small variations in load between the fuels.

Figures 7 and 8 show typical mass fraction burn plots for each of the two fuels, while Figures 29 and 30 show the typical in-cylinder pressure derived information used in this study.

CONCLUSIONS

A comprehensive study of the emissions reduction benefits of a natural gas-derived FT fuel as used in an unmodified direct injection diesel engine was conducted. A set of 12 speed and load points was chosen to generate in-cylinder pressure derived characteristics that then allowed comparison between the combustion and emissions characteristics of the fuels. The following comparisons can be drawn.

The regulated emissions on FT fuel are almost entirely lower than those of D2 (with the exception of HC emissions at some speed and load points). On average, for the 12 speed-load points, HC was reduced by 14%.

On average, CO was reduced by 21% for the FT fuel over D2. The reduction in CO ranged from a low of 3.1% at Point 12 to a maximum of 46% at Point 1. On average, CO₂ was reduced by 4.9% with a range of 3.8 to 6.2%. NOx is reduced, on average, by 20% with the range from 14% for Point 11 to 29% for Point 1. The PN was reduced between 13 and 42% with an average reduction of 31% for the FT compared to the D2.

FT has a shorter ignition delay and longer combustion duration than D2 at the same nominal operating point. FT has an ignition delay that was approximately 14% shorter, on average, than the D2 fuel with a range from 8.8% for Point 11 to 20% for Point 7. The combustion duration was, on average, 14% longer for the FT fuel and ranged from 1.7% for Point 8 to 53% for Point 9. The summation of the ignition delay and combustion duration showed that there was an average 1.1% increase in the combined time for the FT fuel. Point 8 showed a 5.1% decrease in the combined time for FT while Point 9 exhibited a 15% increase in the combined time for the FT.

FT exhibited an average 3.4% lower peak combustion pressure than D2 at the same speed-load point. The location of the peak pressure was generally later for the FT fuel, although it did range from 10% sooner for Point 9 to 13% later for Point 3.

FT displayed a 35% average lower maximum burn rate than D2 for the same speed and load. The FT burn rate ranged from 15% lower for Point 11 to 60% lower for Point 9.

For the same exhaust gas temperature, FT and D2 display the same NOx formation rates, but for the same speed and load, FT displayed a noticeably lower exhaust gas temperature, hence resulting in lower NOx emissions. The exhaust gas temperature reduction for the FT fuel ranged from 9 °C lower for Point 12 to 116 °C lower for Point 2.

In conclusion, while FT derates an unmodified compression ignition engine by a small amount at its highest load settings, the brake specific emissions on FT fuel are significantly lower than on D2. Lower peak incylinder pressures, resulting in lower in-cylinder temperatures, are chiefly responsible for the lower NOx reduction benefits of FT (an average of 20% for the speed and load points considered), while the lower sulfur content of the fuel results in lower PM emissions (an average of 31% lower). These results show great promise in the further reductions of exhaust emissions in an engine with optimized injection timing.

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Table 1 Engine data collected.

Parameter	Abbreviation	Unit
Engine Speed	Speed	RPM
Fuel Injection Pulse Width	FIPW	μς
Fueling Advance	Advance	°BTDC
Exhaust Temperature	ExTemp	°C
Intake Air Temperature	IAT	°C
Manifold Boost Pressure	MAP	kPa
Engine Coolant Temperature	ECT	•℃
Acceleration Pedal Sensor	APS	%
Dynamometer Torque	Torque	Nm
Engine Oil Temperature	EOT	°C
Injection Control Pressure	ICP	ADC
Dilution Tunnel Flow	Vflow	m³/s
Diluted Hydrocarbon Concentrations	HC	ppm
Diluted Carbon Monoxide Concentrations	CO	ppm
Diluted Carbon Dioxide Concentrations	CO ₂	ppm
Diluted Oxides of Nitrogen Concentrations	NOx	ppm
Dilution Tunnel Temperature	VTemp	K
Dilution Tunnel Pressure	VPres	kPa
In-cylinder Pressure	Peak	kPa
Particulate Matter Mass Rate	PM	g/s

Table 2 Fuel properties.

		D2		FT			
Fuel Parameter	ASTM Method	Units	Value	ASTM Method	Units	Value	
Density	D-287	API (Sp.gr.)	37.4 (0.838)	D-4052	Sp. gr.	0.7845	
Aromatics	D-1391	Vol %	24.7	D-5186	Wt. %	0.1	
Sulfur		Wt. %	<0.35%*	D-129	Wt. %	<0.05	
Cetane	D-976	•	48.7	D-613	-	73.7	
Viscosity		Not Reported		D-445	CSt	3.57	
Net Heat of Combustion	D-240	BTU/lb	18513	D-240	BTU/lb	18883	
Carbon	D-5291	Mass %	86.11	D-5291	Mass %	84.91	
Hydrogen	D-5291	Mass %	13.37	D-5291	Mass %	14.94	

^{*} Typical base specification.

Table 3 Speed and load settings. The load is given as the desired set point, with the average D2 measured, and the average FT measured.

Point	Speed		Load (Nm)	
1 01111	(RPM)	Set	D2	FT
i	1300	135	131.4	130.3
2*	1300	542	539.1	538.8
3	1500	271	273.0	267.0
4	1500	542	544.7	541.5
5*	1500	621	621.2	614.7
6	1900	271	266.5	265.2
7	1900	542	541.1	534.9
8*	1900	589	589.1	570.2
9	2200	203	197.1	196.7
10	2200	406	397.6	400.8
11*	2200	567	567.2	550.1
12*	2600	469	469.3	460.9

^{*} Maximum load points.

Table 4 Emissions measurement equipment.

Emission Type	Analyzer Type	Method
NOx	Rosemount Analytical Model 955 NO/NOx	Chemiluminescence (CLD)
	Beckman Industrial Model 868	Non-Dispersive Infrared (NDIR)
co	Rosemount Analytical Model 880A	Non-Dispersive Infrared (NDIR)
HC	Rosemount Analytical Model 402	Flame Ionization Detector (FID)
	Rupprecht & Patashnick TEOM Model 1105	Tapered Element Oscillating Microbalance

Table 5 Combustion derived parameters.

Shorthand Abbreviation	Parameter	Definition
Peak	Peak Pressure Value	Maximum pressure encountered in and in the land
LPP	Location of Peak Pressure	Maximum pressure encountered in each individual cycle (kPa). Location of the maximum pressure encountered (CA°).
IMEPg	Indicated Mean Effective Pressure (gross)	Integrated work for the compression and expansion cycles, divided by the displacement of a single cylinder (kPa)
IgnDel	Ignition Delay	Time in crank angle degrees from fuel injected to the start of the mass fraction burned (CA°).
CombDur	Combustion Duration	Time in crank angle degrees from 10% to 90% of the mass fraction burned (CA°).
LMFB50	Location of Mass Fraction Burned - 50%	Location of 50% of the integrated mass fraction burned curve (CA°).
MaxBum	Maximum Burn Rate	Maximum rate of pressure rise calculated from a 5-pt. central difference (kPa/microsecond).
MaxBurnLoc	Maximum Burn Rate Location	Location of the maximum burn rate (CA°).
MaxTorque	Maximum Torque	Maximum instantaneous torque based on geometric calculation of moment arm and pressure (Nm).
MaxTorqueAngle	Maximum Torque Angle	Location of the maximum torque (CA°).
MixingBurn	Mixing Burn	Measure in crank angle degrees of the time from 50% to 99% of the mass fraction burned (CA°).
MaxQ	Maximum Heat Release (Q)	Maximum value of the instantaneous heat release used to calculate the mass fraction burned (kJ/Crank Angle Degree).
MaxQLoc	Maximum Heat Release (Q) Location	Location of the maximum heat release (CA°).

Table 6 Relative brake specific emissions (with each emission normalized to the maximum value across all tests to each given fuel maximum value).

Point	Point HC		_	co		CO ₂		NOx		PM	
	D2	FT	D2	FT	D2	FT	D2	FT	D2 '	FT	
1	1.00	1.00	0.14	0.09	1.00	1.00	1.00	1.00	0.40		
2*	0.06	0.14	1.00	1.00	0.84	0.85	0.64	0.76		0.38	
3	0.25	0.29	0.03	0.03	0.83	0.85	0.79		1.00	1.00	
4	0.07	0.13	0.17	0.16	0.80			0.89	0.10	0.12	
5*	0.06	0.10	0.37	0.34		0.82	0.72	0.84	0.34	0.32	
6	0.22	0.23	0.04		0.81	0.81	0.65	0.78	0.73	0.67	
7	0.07	0.10		0.03	0.88	0.88	0.71	0.75	0.15	0.14	
8*	0.06		10.0	0.01	0.82	0.84	0.63	0.73	0.14	0.12	
9		0.10	0.02	0.02	0.81	0.82	0.72	0.86	0.14	0.12	
	0.23	0.29	0.06	0.04	0.98	1.00	0.77	0.78	0.25	0.24	
10	0.13	0.14	0.02	0.02	0.86	0.87	0.66	0.71	0.14		
11*	0.07	0.12	0.01	0.02	0.83	0.85	0.64			0.11	
12*	0.09	0.13	0.02	0.02	0.90	0.91		0.77	0.17	0.16	
					0.70	0.91	0.58	0.63	0.35	0.31	

^{*} Maximum load points. Numbers greater than 0.75 are boldfaced.

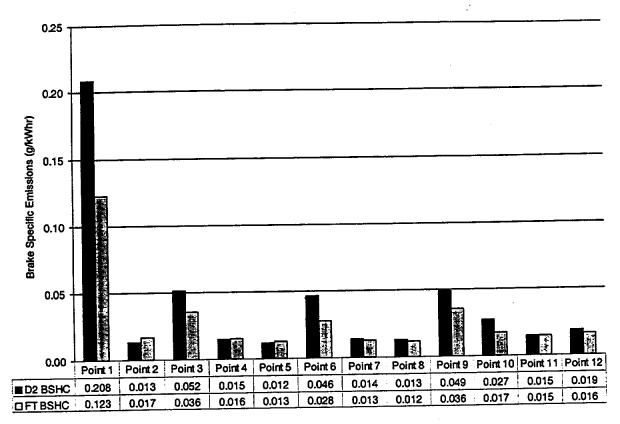


Figure 1 Brake specific HC emissions comparison.

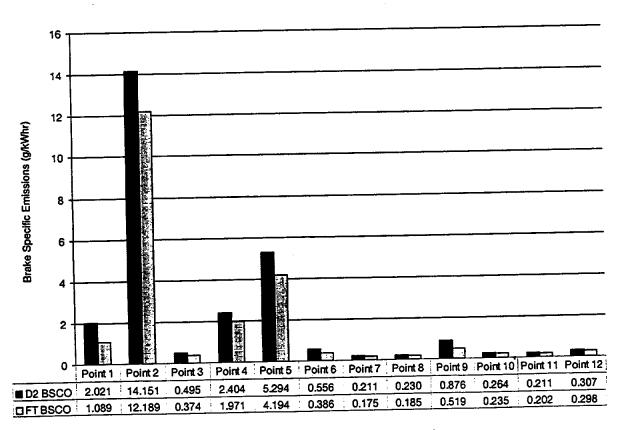


Figure 2 Brake specific CO emissions comparison.

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ABSTRACT

Synthetic diesel fuel can be made from a variety of feedstocks, including coal, natural gas and biomass. Synthetic diesel fuels can have very low sulfur and aromatic content, and excellent autoignition characteristics. Moreover, synthetic diesel fuels may also be economically competitive with California diesel fuel if oduced in large volumes.

Previous engine laboratory and field tests using a heavyduty chassis dynamometer indicate that synthetic diesel fuel made using the Fischer-Tropsch (F-T) catalytic conversion process is a promising alternative fuel because it can be used in unmodified diesel engines, and can reduce exhaust emissions substantially.

The objective of this study was a preliminary assessment of the emissions from older model transit operated on Mossgas synthetic diesel fuel. The study compared emissions from transit buses operating on Federal no. 2 Diesel fuel, Mossgas synthetic diesel (MGSD), and a 50/50 blend of the two fuels. The buses were equipped with unmodified Detroit Diesel 6V92 2-stroke diesel engines. Six 40-foot buses were tested. Three of the buses had recently rebuilt engines and were equipped with an oxidation catalytic converter. Vehicle emissions measurements were performed using West Virginia University's unique transportable chassis dynamometer. The emissions were measured over the Central Business District (CBD) driving cycle.

The buses performed well on both neat and blended MGSD fuel. Three buses without catalytic converters were tested. Compared to their emissions when operating on Federal no. 2 diesel fuel, these buses emitted an average of 5% lower oxides of nitrogen (NOx) and 20% lower particulate matter (PM) when operating on neat MGSD fuel. Catalyst equipped buses emitted an average of 8% lower NOx and 31% lower PM when operating on MGSD than when operating on Federal no. 2 diesel fuel

INTRODUCTION

The Energy Policy Act of 1992 (EPACT) was enacted to stimulate the research, development, and accelerated introduction of alternative fuel technologies in the United States. The objective of EPACT is to reduce the nation's dependence on imported petroleum by pursuing renewable and domestically produced energy resources. Under EPACT, DOE has established programs to promote energy diversity and the displacement of crude oil-based motor fuels.

"Gas-to-liquids" (GTL) process technology is one promising approach for achieving energy diversity [1-7]. A brief history of the Fischer-Tropsch GTL synthetic diesel process was given in a previous paper [8]. There has been heightened interest in GTL technology in recent years, as researchers and industrial firms are demonstrating favorable production economics. GTL fuel and chemical plants are emerging in developing countries. GTL pilot plants are also being developed for remote and off-shore applications to liberate remote and stranded natural gas reserves. F-T and other synthetic diesel fuels may be economically competitive with low aromatic California diesel fuel if produced in large volumes. For a

commercial-scale plant, synthetic fuel price estimates range from \$20 to \$25 per barrel of product [2,5-7].

Fischer-Tropsch synthetic diesel fuel is typically synthesized using a three-step procedure [2-6]. First a synthesis gas is produced from the feedstock, F-T catalysis is then used to convert this synthesis gas into liquid hydrocarbons, and finally the resulting synthetic crude is upgraded using standard hydrotreating and isomerization processes and fractionated into middle distillate fuels. This process can be used to create a variety of fuel properties depending on the process technology and streams being blended. Generally, synthetic diesel fuels have favorable characteristics for use in compression ignition engines including:

- Liquid phase at ambient conditions
- Miscible in conventional petroleum-derived diesel
- Good autoignition characteristics (cetane number of 50-75 typically)
- Low sulfur (typically less than 10 ppm)
- Low aromatics (less than 3 ol% possible)
- Energy density comparable to conventional diesel
- Fuel tank flammability similar to conventional diesel
- Suitable for use in unmodified diesel engines
- Transportable as a liquid in existing petroleum infrastructure.

Due in part to the success of previous engine and chassis based testing [9-12], synthetic diesel is being considered as a candidate fuel for the DOE/NREL Alternative Fuel Truck and Bus Evaluation Projects [13].

TEST FUELS

Three test fuels were used for the bus tests:

- Federal (49-state) no. 2 diesel fuel
- 100% Mossgas synthetic diesel with fuel lubricity additive
- 50:50% Mossgas synthetic diesel:Federal no. 2 diesel with fuel lubricity additive

The synthetic diesel fuel for this study was produced using the Mossgas conversion of olefins to distillate ("COD") process. Mossgas produces a range of automotive fuel products and chemicals using a natural gas feedstock obtained by pipeline from their off-shore production platform in Mossel Bay, South Africa. The natural gas is reformed to synthesis gas consisting of hydrogen and carbon monoxide. The synthesis gas is chemically converted using high temperature Fischer-Tropsch catalysis to produce olefins and automotive fuel components for commercial markets.

The light olefins that remain from the Fischer-Tropsch conversion, such as propene, butene, pentene and

hexene, were used to synthesize the test fuel used in this study. These light olefins were catalytically oligomerized over a zeolite catalyst to form gasoline and distillate. The resulting product was then hydrotreated. Mossgas uses the COD process to produce commercial specialty fuel and blendstocks.

The properties of the Mossgas synthetic diesel fuel and the Federal no. 2 diesel fuel used in this study are shown in Table 1. The Mossgas fuel had no detectable sulfur, and a cetane number of about 50. The aromatic content was 10% by volume, which is higher than that of a typical Fischer-Tropsch diesel. The cold flow properties of the Mossgas fuel were excellent with a pour point and cloud point below —60 degrees Celsius. A commercially available lubricity improver (Paradyne 655 at 200 ppm treat rate) was added to meet acceptable lubricity levels.

The Federal no. 2 diesel used in the study had a relatively low sulfur content of 0.02% by weight. This is much lower than the standard of 0.05% and lower than the 0.03% to 0.035% sulfur content typically found in Federal diesel.

VEHICLE TESTING

TEST VEHICLES – The buses used for the testing were loaned to the project by the Port Authority of Allegheny County ("PaTransit"). They were removed from revenue service in Pittsburgh, PA for the emissions measurements. The 40-foot buses were 1991 model year made by Orion Bus Industries and equipped with 1991 model year Detribiesel Corporation (DDC) 6V92 two-stroke diesel engines. One of the test buses is shown in Figure 1.



Figure 1: One of the Pittsburgh transit buses used for the emissions measurements.

Table 1: Test Fuel Properties

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	<u> </u>		100% MGSD	100% MGSD	Federal
Analysis	ASTM	Units	(Mossgas Data)	(SwRI Data)	Diesel Fuel
Flash Point			[14]	[15]	[16]
Cloud Point	D93	°C	100	97	
	D2550	°C		<-60	
Water content	D1744	vol%	0.01		
Sediment by extraction	D473	mass%	<0.01		
Water and Sediment	D1796	vol%		0	
Carbon Residue on 10% residue	D4530	wt%	0.09		
Carbon Residue on 10% distillation residue	D524	%		0.1	
Ash	D482	wt%	<0.01		
Distillation	D86	°C	10.01		
IBP				229.9	188
10%	1		1	235.3	212
50%				254.7	256
90%	•		321.1	323.7	307
FBP			360.8	361.2	331
Kinematic Viscosity	D445	cSt @ 40°C	2.974	2.98	1 331
Sulfur	D2622	mass%	<0.001	2.00	
Sulfur	D5453	ppm	-0.001	<5	
Sulfur	D4294	wt%			0.02
Corrosion, 100°C for 3 hours	D130	Rating	1A		0.02
Cetane Number	D613	iteurg	51.4	40.0	
Cetane Index	D4737		31.4	48.9	ļ
	D4052/		<u> </u>		48.7
Density @ 20°C	D1298	kg/l	0.8007	0.8042	
API Gravity @ 15.6°C	D287	^o API		44.0	37.4
Cold Filter Plugging Point	IP309	°C	<-35		
Pour Point	D97	ိင		<-60	
SFC Aromatics	D5186	mass%			
Total Aromatics PNA				9.18	
FIA	D1319	vol%		0.21	
Aromatic	פונוט	VO170			
Olefins					24.7
Saturate]		1.5
Aromatics	IP391	vol%	10.1	· · · · · · · · · · · · · · · · · · ·	73.8
Gum Content	D381	mg/100ml	10.1		
Unwashed	5501	my/icom]	0.0	1
Washed]			8.8	
Lubricity SLBOCLE	D6078	grams	 	0.4	
Neat Fuel	50010	भुग्याह		1050	1
With Paradyne additive]	1950	
Lubricity HFRR	D6079	micron	 	3800	
Neat Fuel	20078	maon		600	1
With Paradyne additive				600 355	
Oxidation Stability	D2274	mg/100 ml	0.3	255]
Carbon/Hydrogen	D5291	mg/100 mi mass%	U.3		
Carbon	03281	11185570		00.00	
Hydrogen				83.98	86.11
Nitrogen			1	14.43	13.37
Residual					<0.03
Oxygen (by diff)	Į į			1.50]
Heat of Combustion	D240			1.59	
Gross	2270	Btu/gal		124 712	407.000
Net]	owyai		134,712	137,609
				125,878	129,147



The DDC 6V92 is a 2-stroke, vee-configuration, 6 cylinder, 9.05 liter, turbocharged and aftercooled diesel engine with electronic unit fuel injectors. The Pittsburgh bus engines were rated to 253 horsepower (at 2100 rpm) and 880 ft-lb of torque (at 1200 rpm).

Three of the six buses used in this study used engines with high mileage accumulation (typically over 350,000 miles) and were not equipped with exhaust gas aftertreatment. The other three buses had engines that were recently rebuilt according to the Environmental Protection Agency's Urban Bus Retrofit/Rebuild Program and were fitted with an oxidation catalytic converter manufactured by Engine Control Systems Ltd. Bus number 2029 was tested early in the study without a catalyst. It was then fitted with a rebuilt engine and a catalytic converter and retested. The test buses were not modified in any way for the Mossgas synthetic diesel fuel.

CHASSIS EMISSIONS TESTING - West Virginia University (WVU) measured emissions for this study using one of its transportable emissions laboratories located at the WVU home site in Morgantown, WV. The transportable laboratory consists of a heavy-duty chassis dynamometer and an emissions measurement facility. Design details of the laboratory and previous emissions measurements using the laboratory have been presented in several previous reports [17-25].

Chassis Dynamometer — The dynamometer equipment is mounted on a fifth wheel semi-trailer for portability. Upon arriving at the test site, the wheels of the trailer are removed and the trailer is lowered to the ground. The test vehicle is driven onto two sets of free running rollers mounted in the trailer bed. Power is transferred from the test vehicle to the dynamometer through hub adapters that are bolted to the drive wheels. The inertia weight of the bus is simulated by a set of flywheels. The road load is applied to the test vehicle using air-cooled eddy current power absorbers. Figure 2 shows one of the test buses mounted on the dynamometer.

Emissions Measurements – The emissions measurement system uses a 45.7 cm (18 in.) diameter, 6.1 m (20 ft.) long exhaust dilution tunnel mounted atop the box trailer that houses the emissions measuring equipment. Two fans and critical flow venturis control the flow rate in the dilution tunnel.

Carbon monoxide (CO), carbon dioxide (CO₂), oxides of nitrogen (NO_x), and total hydrocarbons (THC) are measured continuously throughout the test. Particulate matter (PM) is captured on a filter and weighed. Bag samples are collected and analyzed for background correction.

Test Method – The buses were tested using the Central Business District (CBD) driving cycle described in SAE Recommended Practice J1376. The CBD driving cycle was developed by the Federal Transit Administration to represent the operation of a transit bus in a downtown business district. The cycle, shown in Figure 3, consists of



Figure 2: One of the PaTransit buses on the WVU transportable chassis dynamometer

fourteen identical acceleration, cruise, and deceleration cycles. A short idle time was added before and after the vehicle activity to aid data gathering in the light of sampling delay times [26]. The cruise sections occur at 32 km/hr (20 mph). Transit bus emissions measurements using this driving cycle have been reported in many previous papers [for example, 22, 27-29].

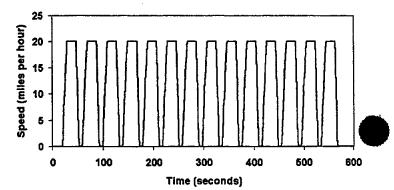


Figure 3: The Central Business District (CBD) driving cycle.

<u>Tests Performed</u> – Three buses with rebuilt engines and equipped with catalytic converters and three buses without catalytic converters were tested. The emissions from each bus were measured while the bus operated on each of the three test fuels. Between measurements with different fuels, the bus' fuel system was emptied and flushed with the new fuel type. The emission tests performed are summarized in Table 2.

Table 2: Summary of Emissions Tests Performed

	Fuel	Number of Tests
Buses with	No. 2 Diesel	3
rebuilt engines and	100% MGSD	3
catalytic converters	50% MGSD	3
Buses without	No. 2 Diesel	3
catalytic converters	100% MGSD	3
•	50% MGSD	3
	<u> </u>	Total = 18

RESULTS

Drivers could not detect a performance difference between buses operating on the Mossgas synthetic diesel and the Federal no. 2 diesel fuel-over the CBD driving cycle. The rerage emissions results are summarized in Table 3. At east three measurements were taken and averaged for each result presented in the table.

EFFECT OF TEST FUEL - Three buses equipped with rebuilt engines and catalytic converters were tested on the three test fuels. The results of these tests are shown in the bar charts of Figure 4. Each chart shows results for each bus and the average of all three buses. Substituting 100% MGSD fuel in place of no. 2 diesel fuel led to lower average levels of all four emissions measured. NO_x was

reduced by an average of 8%, PM was reduced by an average of 31%, CO was reduced by an average of 49%, and HC was reduced by an average of 35%. The average NO $_{\rm x}$ reduction with a 50:50 blend of no. 2 diesel and MGSD was substantially more than half of the reduction with 100% MGSD fuel. The PM reduction with the blend was approximately half of the reduction measured with 100% MGSD fuel.

With the exception of the hydrocarbon emissions from bus 2029, all buses followed the same trend of progressively decreasing emissions with 50% and 100% Mossgas synthetic diesel.

Table 3: Average emissions (in grams per mile) and fuel mileage from buses tested on federal No. 2 diesel, Mossgas synthetic diesel (MGSD), and a 50:50 blend of the two fuels.

	Fuel	Bus	00	110		5.4			
Buses with		Number	CO	NOx	HC	PM	CO₂	MPG*	Btu/mile
1	No. 2 Diesel	2025	1.96	34.51	0.75	1.23	4355	2.33	55713
rebuilt engines and	No. 2 Diesel	2029	1.07	26.91	0.39	1.89	4458	2.28	56995
catalytic converters	No. 2 Diesel	2048	2.11	29.71	0.75	1.12	3451	2.94	44159
	Averages:		1.71	30.38	0.63	1.41	4088	2.52	52289
	50% MGSD	2025	1.34	31.93	0.54	1.14	4360	2.20	57589
÷	50% MGSD	2029	0.81	26.40	0.40	1.59	4346	2.21	57391
	50% MGSD	2048	1.51	27.69	0.59	0.83	3381	2.84	44672
	Averages:		1.22	28.67	0.51	1.19	4029	2.42	53217
	100% MGSD	2025	1.02	31.37	0.44	1.01	4206	2.19	56272
	100% MGSD	2029	0.75	26.10	0.29	1.16	4181	2.21	55928
	100% MGSD	2048	0.82	26.53	0.49	0.76	3338	2.77	44659
	Averages:		0.87	28.00	0.41	0.97	3908	2.39	52286
Buses without	No. 2 Diesel	2029	11.73	35.85	1.82	1.79	4328	2.34	55598
catalytic converters	No. 2 Diesel	2030	6.65	34.88	2.11	1.18	4149	2.44	53221
	No. 2 Diesel	2034	40.42	26.26	1.31	9.03	4900	2.05	63468
	Averages:		19.60	32.33	1.75	4.00	4459	2.28	57429
	50% MGSD	2029	10.33	32.23	1.88	1.52	4348	2.20	57601
	50% MGSD	2030	6.26	33.93	2.03	1.13	4099	2.34	54244
	50% MGSD	2034	37.91	26.02	0.99	8.61	4704	2.02	62887
	Averages:		18.16	30.72	1.63	3.75	4383	2.18	58274
	100% MGSD	2029	11.02	33.37	1.72	1.34	4392	2.09	58963
	100% MGSD	2030	5.73	32.92	1.75	1.16	4133	2.23	55391
	100% MGSD	2034	26.52	25.64	0.72	7.07	4639	1.97	62596
	Averages:		14.42	30.64	1.40	3.19	4388	2.10	58984

^{*} Miles per liquid gallon (not corrected for energy content)

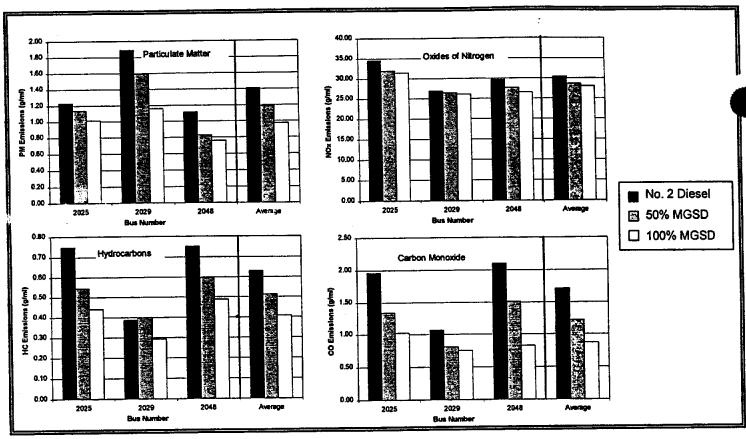


Figure 4: Emissions results from buses with rebuilt engines and catalytic converters

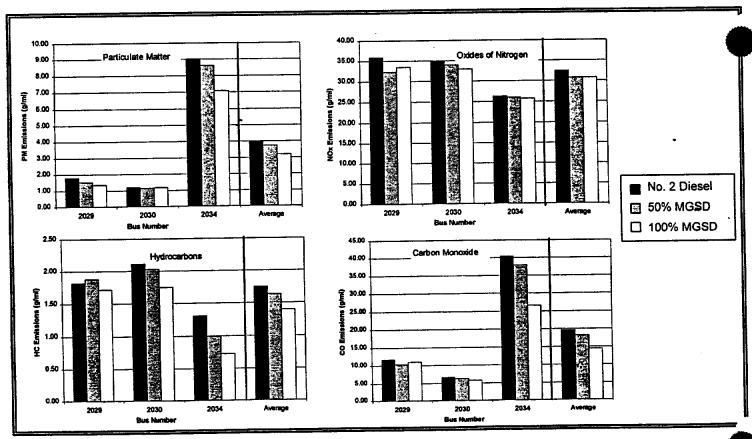


Figure 5: Emissions results from buses without catalytic converters

Three buses with high mileage engines and no catalytic converters were also tested. The results of these tests are shown in the bar charts of Figure 5. Substituting 100% Mossgas synthetic diesel fuel in place of Federal no. 2 esel fuel in these buses also led to lower average levels of all four emissions measured. NO, was reduced by an average of 5%, PM was reduced by an average of 20%. CO was reduced by an average of 26%, and HC was reduced by an average of 20%. In this case, The average NO₂ reduction with a 50:50 blend of no. 2 diesel and MGSD was nearly identical to the reduction with 100% MGSD. This result agrees with an earlier study by the authors on class 8 trucks using Shell Middle Distillate F-T fuel [8]. In contrast, the PM reduction with the blend was only about a quarter of the reduction measured with 100% MGSD fuel.

Bus number 2034 had dramatically higher PM and CO emissions and somewhat lower NOx and HC emissions than buses 2029 and 2030. Although buses 2029 and 2030 had similar fuel consumption (within about 4%), the fuel consumption of bus 2034 on Federal no. 2 diesel was somewhat higher (about 16% higher than the average of buses 2029 and 2030). The higher fuel consumption and lower NOx indicates that the injection timing in bus 2034 may be retarded relative to manufacturer specifications. Note that much of the average PM reduction with MGSD in this set of buses is due to the large reduction in PM from bus 2034.

"When tested on 50% MGSD, the emissions trends of bus umber 2029 (without a catalyst) were different than the other two non-catalyst buses for NOx, HC, and CO. These trends can be seen clearly in Figure 5. The cause of this anomaly is unknown.

EFFECT OF REBUILT ENGINES AND CATALYST - The average emissions from buses with rebuilt engines and catalytic converters are compared to emissions from buses with older engines and no catalytic converters in Figures 6 and 7. The buses with rebuilt engines and catalysts had dramatically lower CO, HC and PM emissions than those with older engines and no catalyst. Most of this reduction is likely due to the oxidizing effect of the catalyst on CO, HC, and the soluble organic fraction of the PM emissions.

Also apparent from Figures 6 and 7 is that NOx emissions were reduced somewhat in the buses with rebuilt engines and catalytic converters. The NOx reduction cannot be attributed to the catalyst. The emission reductions from buses with rebuilt engines and catalysts followed the same trends in all buses with both MGSD and Federal no. 2 diesel.

Continuous gaseous emission rates were measured during the tests. Although not directly relevant to the comparison of fuels, an interesting trend in the continuous data varrants mentioning. Buses with oxidation catalytic converters had decreasing HC and CO emissions over the course of the CBD test cycle. Typical continuous HC and CO for a catalyst-equipped bus are shown in Figures 8

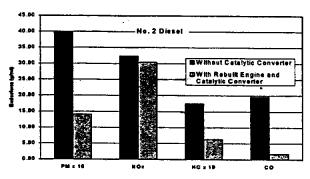


Figure 6: Average emissions results from buses with rebuilt engines and catalytic converters compared to buses without catalytic converters while operating on no. 2 diesel fuel.

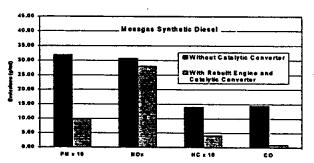


Figure 7: Average emissions results from buses with rebuilt engines and catalytic converters compared to buses with out catalytic converters while operating on Mossgas synthetic diesel fuel.

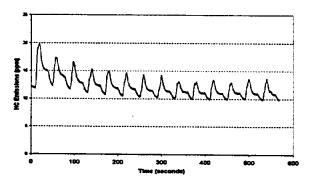


Figure 8: Continuous HC emissions over the CBD cycle from a bus with rebuilt engine and catalytic converter.

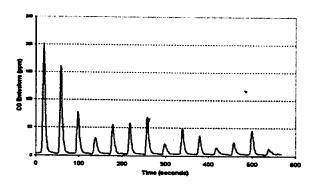


Figure 9: Continuous CO emissions over the CBD cycle from a bus with rebuilt engine and catalytic converter.

and 9. This trend was not observed in buses without catalysts.

Figures 8 and 9 clearly illustrate that the HC and CO drop progressively over the cycle. The WVU protocol for the CBD test cycle includes three additional peaks of the CBD just prior to the actual test data shown here, so the catalyst has already seen some exhaust warming. These results indicate that a test facility that did not employ the warm-up ramps would see higher average HC and CO emissions than measured in this study. This suggests a need for more precisely defined heavy duty vehicle chassis testing protocols to avoid measurement differences between facilities.

FUEL CONSUMPTION – For each of the buses tested, the fuel consumption (in Btu/mile) was not strongly affected by the fuel type. No more than a 3% deviation from the average fuel consumption occurred on any bus. The trends in this small variation were mixed – the MGSD lead to higher fuel consumption in four buses and lower fuel consumption in two buses. The bus-to-bus variability was much greater than the fuel effect. Fuel consumption of no. 2 diesel fuel differed by as much as 23% between catalyst equipped buses and 16% between buses without catalysts.

CONCLUSIONS

- The use of Mossgas synthetic diesel fuel and the use of rebuilt engines and catalysts according to the EPA Urban Bus Retrofit/Rebuild Program both show promise for reducing emissions from older transit buses using Detroit Diesel 6V92 engines.
- The Mossgas synthetic diesel fuel had properties conducive to low emissions, including no detectable sulfur, and an aromatic content of about 10% by volume. The Mossgas synthetic diesel also had excellent cold flow properties.
- Drivers could not detect a performance difference between buses operating on the Mossgas synthetic diesel and the Federal no. 2 diesel fuel over the CBD driving cycle.
- Use of Mossgas synthetic diesel in place of Federal no. 2 diesel in the test buses led to lower levels of all four regulated emissions measured. For the buses with rebuilt engines and oxidation catalytic converters, oxides of nitrogen were reduced by an average of 8%, particulate matter was reduced by an average of 31%, carbon monoxide was reduced by an average of 35%, and total hydrocarbon emissions were reduced by an average of 49%.
- The variation of fuel consumption with test fuel was less than 3% and was much smaller than the bus-tobus fuel consumption variation.

 More precisely defined heavy-duty vehicle chassis dynamometer testing protocols are needed to avoid measurement differences between facilities due to catalyst warm-up.

ACKNOWLEDGMENTS

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

CBD - Central Business District (driving cycle)

CO - Carbon Monoxide

COD - Conversion of Olefins to Distillate

DDC - Detroit Diesel Corporation

DOE - U.S. Department of Energy

EPA - Environmental Protection Agency

EPACT - Energy Policy Act of 1992

FBP - Final Boiling Point

FIA - Fluorescent Indicator Adsorption

F-T diesel - Fischer-Tropsch diesel

FTP - Federal Test Procedure

GTL - Gas-to-liquids

HC - Hydrocarbons

HFRR - High Frequency Reciprocating Rig

IBP - Initial Boiling Point

MGSD - Mossgas synthetic diesel

NO_x – Oxides of Nitrogen

NREL - National Renewable Energy Laboratory

PM - Particulate Matter

ppm - parts per million

SFC - Supercritical Fluid Chromatography

SLBOCLE - Scuffing Load Ball On Cylinder

Lubricity Evaluator

THC - Total Hydrocarbons

WVU - West Virginia University

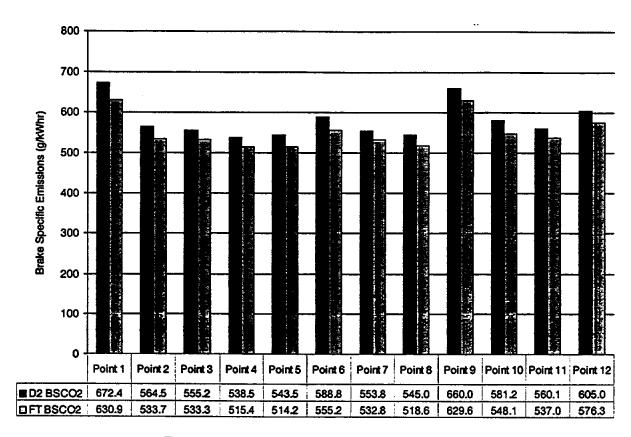


Figure 3 Brake specific CO₂ emissions comparison.

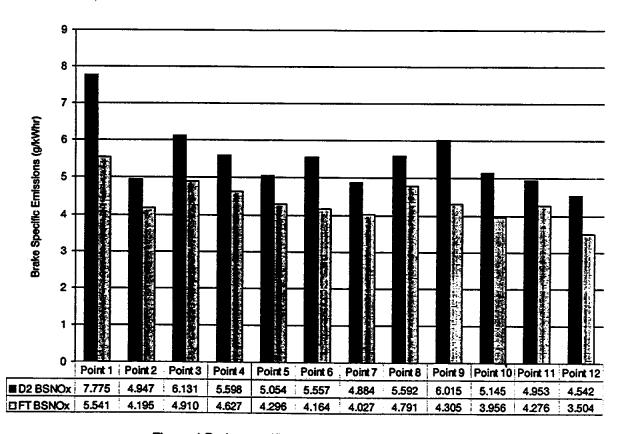


Figure 4 Brake specific NOx emissions comparison.

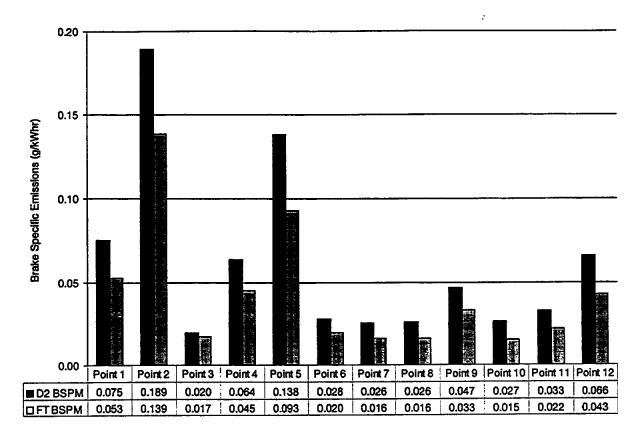


Figure 5 Brake specific PM emissions comparison.

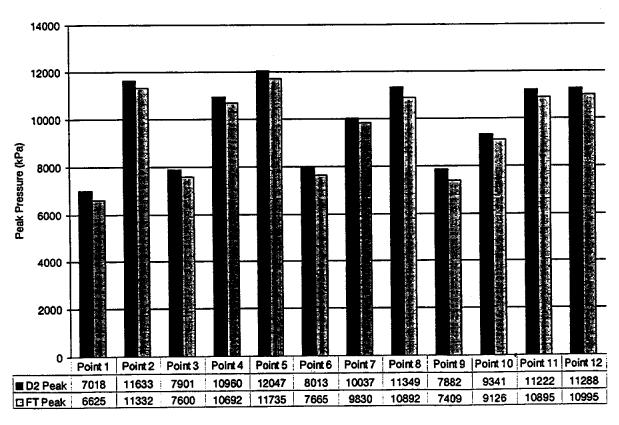


Figure 6 Peak combustion pressure comparison.

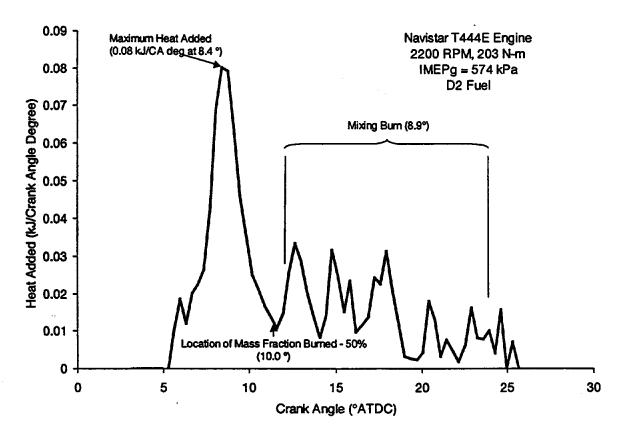


Figure 7 Mass fraction burn information for D2.

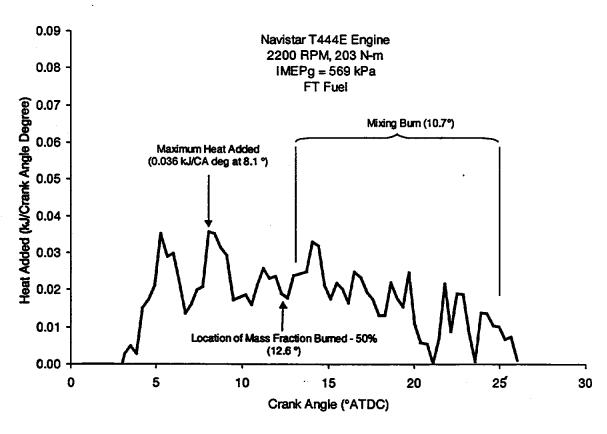


Figure 8 Mass fraction burn information for FT.

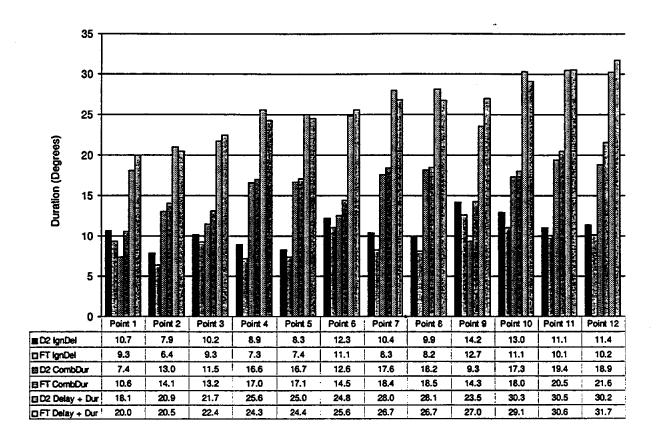


Figure 9 Ignition delay and combustion duration comparison.

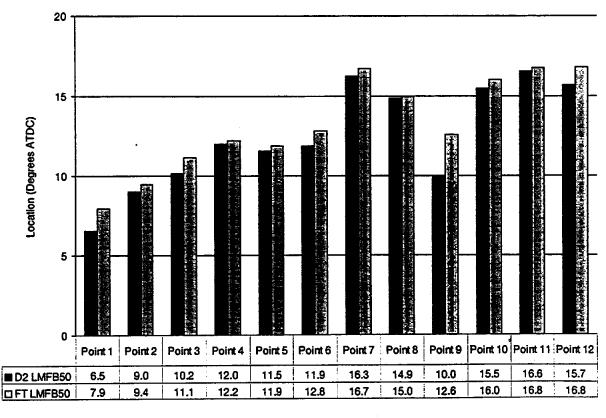


Figure 10 Location of mass fraction burned-50% comparison.

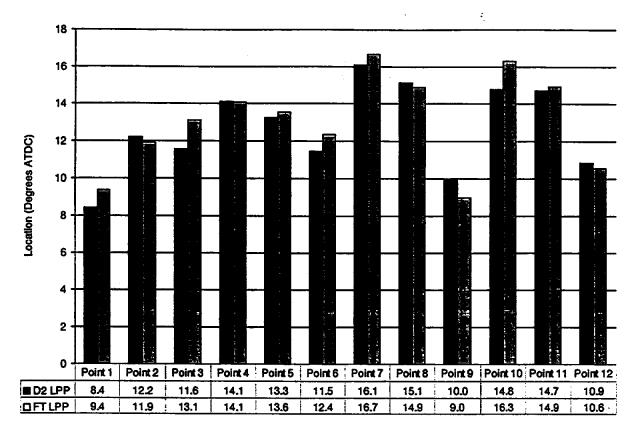


Figure 11 Location of peak combustion pressure comparison.

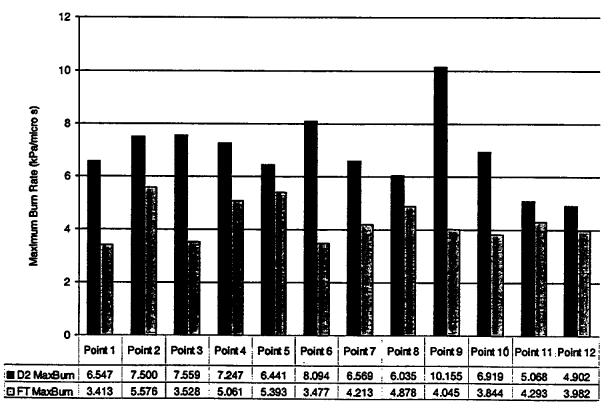


Figure 12 Maximum burn rate comparison.

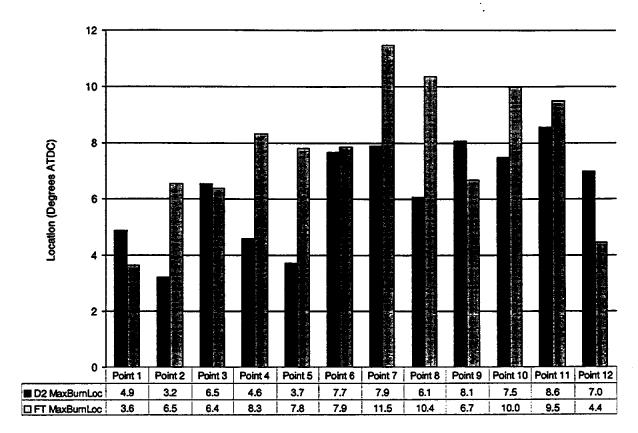


Figure 13 Maximum burn location.

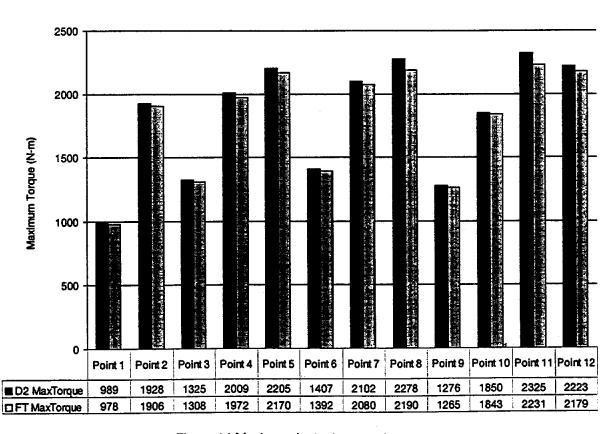


Figure 14 Maximum instantaneous torque.

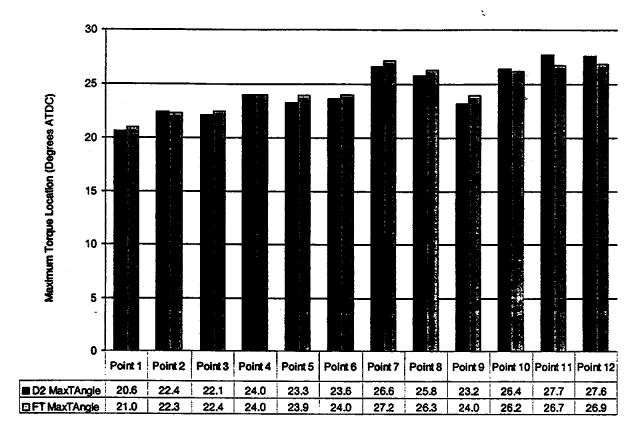


Figure 15 Location of maximum torque.

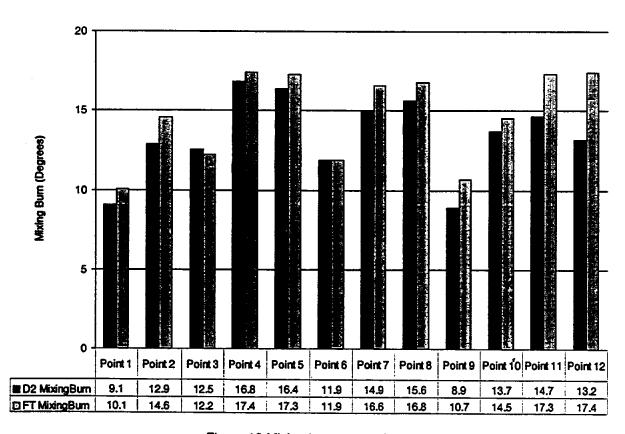


Figure 16 Mixing burn comparison.

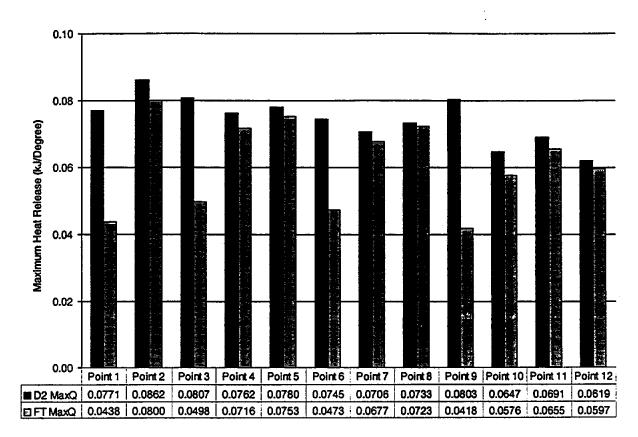


Figure 17 Maximum heat release.

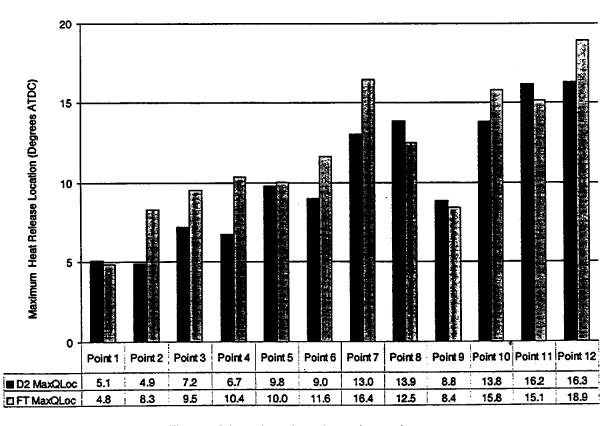


Figure 18 Location of maximum heat release.

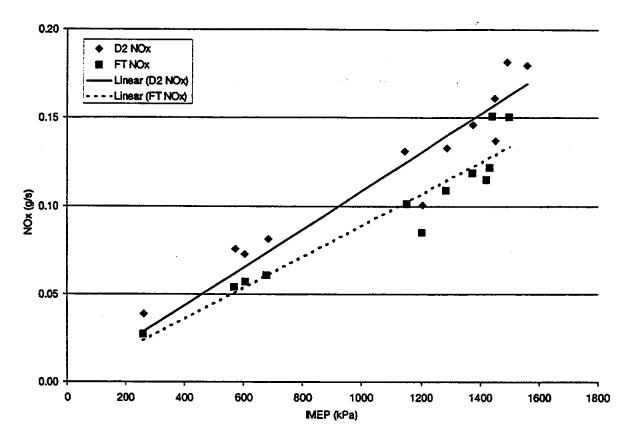


Figure 19 Comparison between NOx and IMEP.

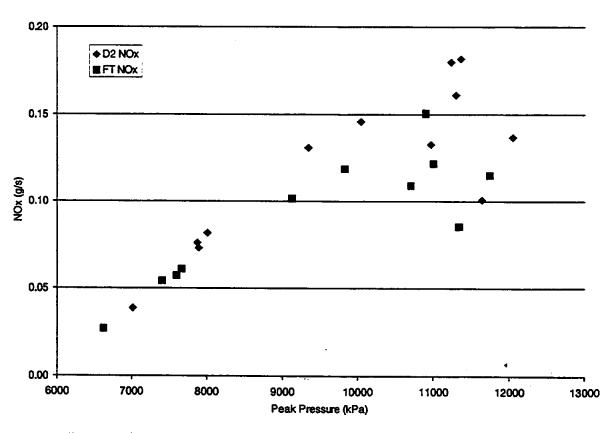


Figure 20 Comparison between NOx and peak in-cylinder combustion pressure.

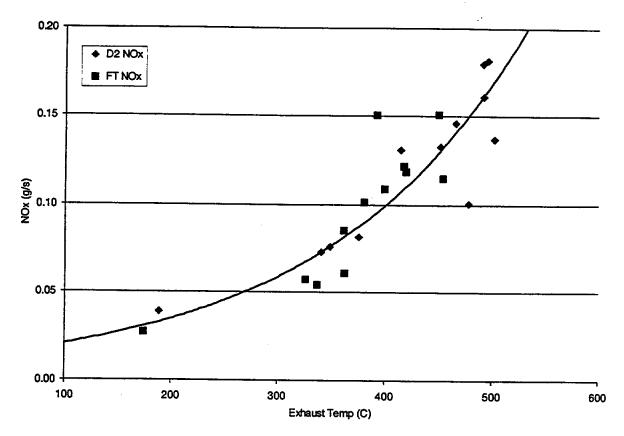


Figure 21 Comparison between NOx and exhaust temperature with an exponential curve fit (all points).

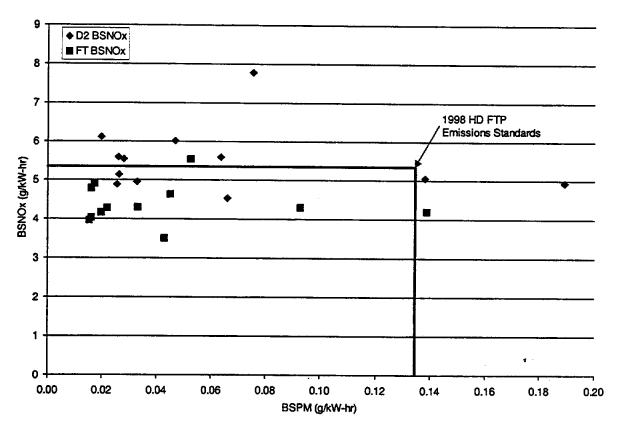


Figure 22 NOx and PM trade-off.

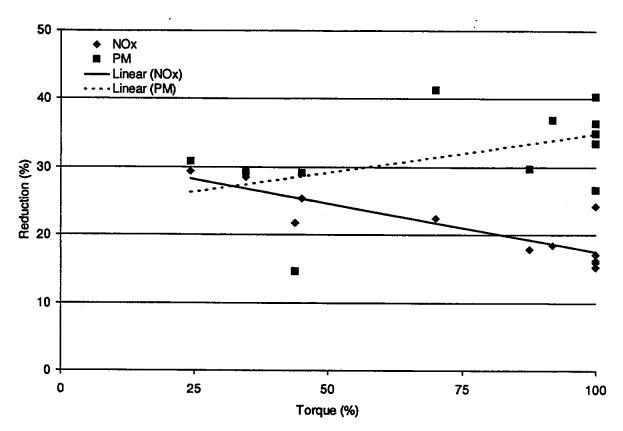


Figure 23 FT NOx and PM reduction, relative to D2, as a function of percentage of full-load torque at a given speed.

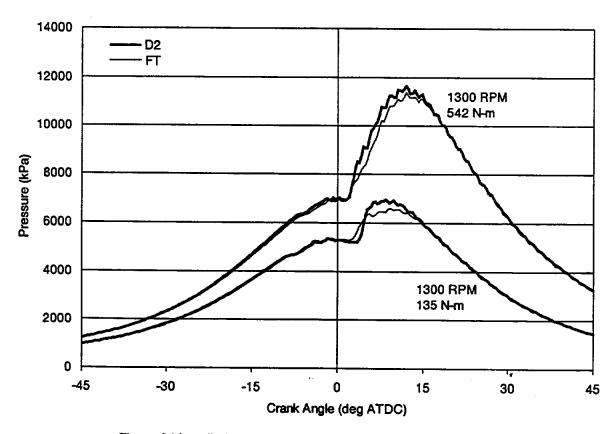


Figure 24 In-cylinder pressure profile comparison at 1300 RPM.

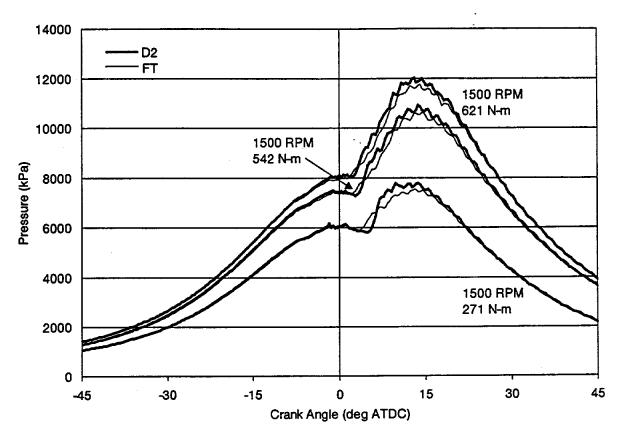


Figure 25 Pressure profile comparison at 1500 RPM.

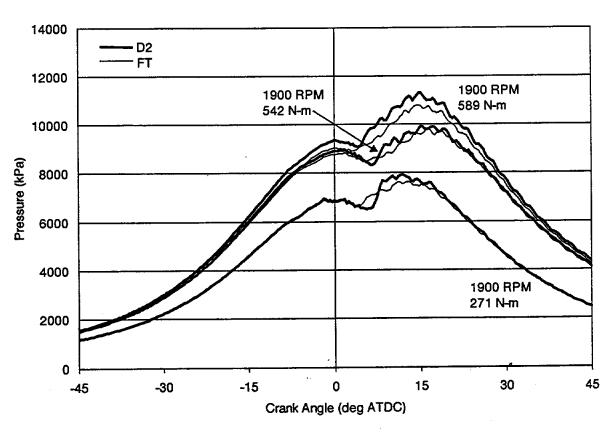


Figure 26 Pressure profile comparison at 1900 RPM.

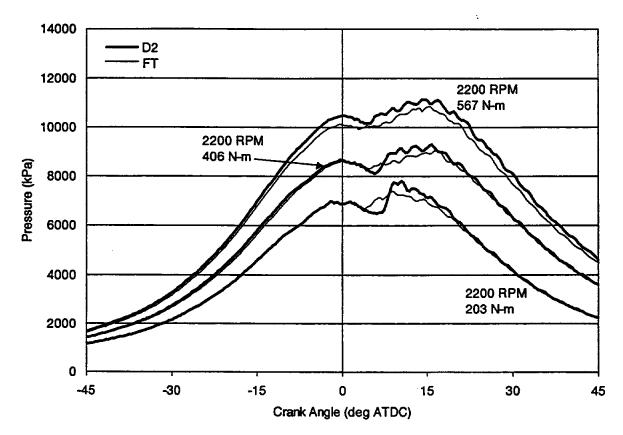


Figure 27 Pressure profile comparison at 2200 RPM.

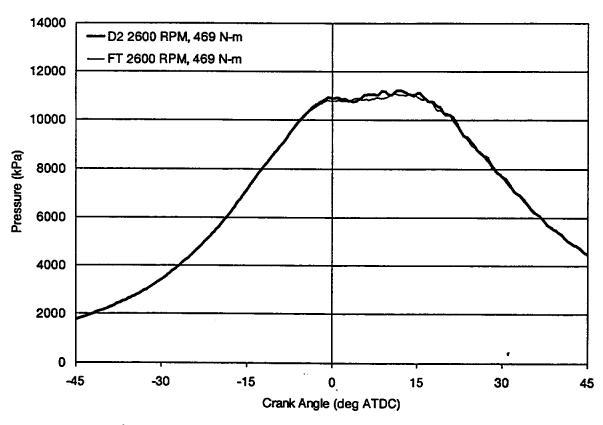


Figure 28 Pressure profile comparison at 2600 RPM.

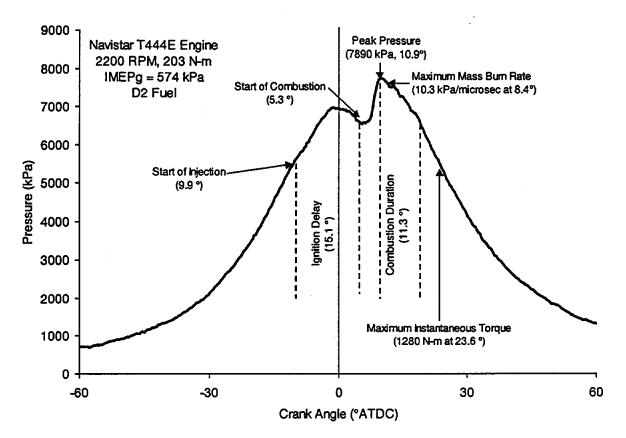


Figure 29 Pressure information for D2.

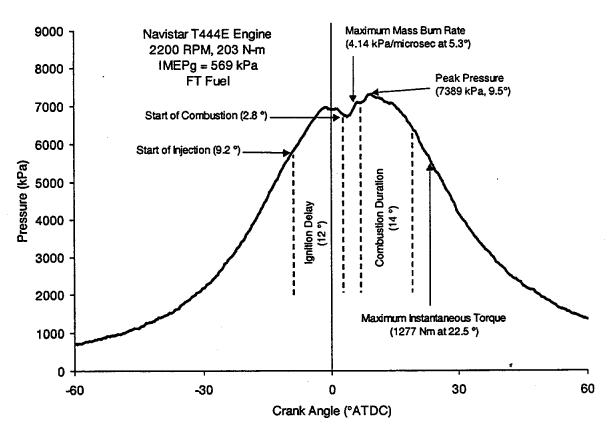


Figure 30 Pressure information for FT.

Type Performance of Fischer-Tropsch Liquids (FTL) in Modified Off-Highway Diesel Engine Test Cycle

G. J. Suppes, C. J. Lula, M. L. Burkhart and J. D. Swearingen
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ABSTRACT

Fischer-Tropsch (FT) conversion of gasification products to liquid hydrocarbon fuel commonly includes FT synthesis followed by mild refining of the FT synthetic oil into diesel, kerosene, and naphtha, each defined by a specific boiling range. These FT products are derived typically by mixing condensable gaseous reactor effluent ($-C_5-C_{20}$) with hydrocracked liquid reactor effluent ($-C_{20+}$). This mixture of FT liquids (FTL), is then hydrotreated and distilled to yield the desired products.

This paper evaluates compression-ignition engine performance during preliminary tests of the condensable gaseous reactor effluent (~C₅-C₂₀) portion of the (FTL) from a Syntroleum Corporation plant. Engine operability, maximum torque, fuel economy and emissions were evaluated for both FTL and mixtures of FTL with gasoline, hexanes, diethyl ether, and ethanol. Emphasis was placed on particulate and NO_x emissions. However, hydrocarbon, carbon dioxide, and oxygen concentrations were also followed.

Engine tests were performed with neat FTL, as well as with FTL formulations containing (1) 25% gasoline; (2) 25% hexanes; (3) 20%, 25%, and 33% of a equal volume mixture of ethanol and diethyl ether; and (4) 20% and 25% ethanol. Performances were compared to US 1D and US 2D diesels. A three-mode test sequence was performed consistent with heavy duty diesel engine applications and each of the fuels met or exceeded goals on reduced emissions and operability of the unmodified engine. Significant emission performance advantages were observed with several of these formulations.

INTRODUCTION

Fischer-Tropsch (FT) synthesis can be used to provide refinery feedstock for producing high-quality compressionignition fuels[1, 2]. The high cetane numbers and low

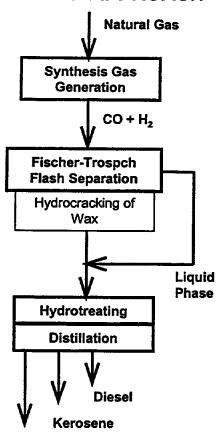
aromatic contents of these compression-ignition fuels lead to reduced CO, hydrocarbons, particulate matter and NO_x [3, 4, 5, 6]. Today, production from remote natural gas is receiving the most interest, but production from coal, biomass, and municipal solid waste is also possible. Low emission characteristics combined with the ability to produce synthetic oil from numerous indigenous carbon resources could make FT synthesis a most valuable technology in the 21st century.

The conventional approach of the FT fuels requires 3-steps (Figure 1). The 1st step generates synthesis gas (CO and H₂) that is converted in the FT reactor (2nd step) to principally straight-chain hydrocarbons and water. At room temperature the hydrocarbons separate into a liquid and solid phase. The 3nd step of typical FT-fuel production consists of 1) hydrocracking the solid phase (wax) to liquid, 2) hydrotreating the FT liquids (FTL), and 3) distilling the FTL into diesel, kerosene, and naphtha components (Figure 1a).

FT diesel is defined by an initial and final boiling point range. The choice of boiling point determines the proportion of each barrel of FTL produced that may be used as diesel fuel. Because diesel is worth considerably more than naphtha in the fuel markets, there is economic incentive to increase the portion of the FTL (broaden the boiling range) that may be used in a diesel blend or as a diesel substitute.

The goal of this investigation was to assess the efficacy of a selected portion of the condensable gaseous reactor effluent (${\sim}C_5{\sim}C_{20}$) from a Syntroleum Corporation plant for use as vehicular fuels. Engine operability, maximum torque, fuel economy and emissions were evaluated for both FTL and mixtures of FTL with gasoline, hexanes, diethyl ether, and ethanol. Emphasis was placed on particulate and NO_x emissions. However, hydrocarbon, carbon dioxide, and oxygen concentrations were also followed.

CONVENTIONAL 3-STEP APPROACH



Naphtha

Figure 1. The conventional 3-step configuration for Fisher Tropsch fuel production.

BACKGROUND

Although diesel has a wide range of properties and specifications, a CI fuel need only meet a few performance criteria for satisfactory to excellent performance. One of these criteria is low corrosivity toward hardened metal injector parts; this is not expected to be a problem since FTL is comprised mostly of hydrocarbons. Other necessary performance criteria are as follows:

- 1. Engine Operability and Emissions. Engine operability is the ultimate test for a fuel. Operability with low emissions is preferred. Preferred fuels would have lower NO_x and particulate emissions than US 2D fuel to meet trends in EPA regulations[7].
- 2. <u>Cetane Number.</u> Cetane numbers correlate directly with fuel ignition and related engine operability. Premeium fuels have cetane numbers greater than 47[8]. ASTM standard D 613 defines the cetane number.
- 3. <u>Pour/Cloud/Cold Flow Point Temperatures.</u> Since vehicles are typically not equipped with heaters for the fuel delivery system, a diesel fuel preferably should flow

under the force of gravity to the pump intake in the fuel tank and then flow through the fuel delivery system. The pour point temperature is representative of the temperature where flow stops. Reductions in pour point temperatures translate to larger potential fuel markets by inclusion of markets at cooler geographical regions and during cooler periods of the year. It is desirable to have fuels with low pour point temperatures, preferably lower than -20 °C in winter and 0 °C in summer. ASTM standards D 97, D 2500, and D 4539 characterize the low temperature operability of CI fuels. The pour point (D 97) is the least stringent of these tests. Additives such as UI8094 and Cold Flow are designed to suppress pour point and flow point temperatures.

- 4. <u>Viscosity</u>. The plungers of diesel fuel injectors are able to generate high pressures only if the fuel does not leak through the low tolerance surface between the plunger and bushing. Low viscosities result in fuel loss and the inability to generate high pressures while high viscosities lead to excessively high pressures before attaining sufficient fuel flow through the injector tips. The viscosity of a fuel must meet engine manufacturers' specifications for proper performance. The standard kinematic viscosity range for diesel fuels is between 1.9 to 4.1 mm²/s at 40°C.
- 5. <u>Lubricity.</u> Diesel fuel injectors rely on the lubricity of the fuel to minimize wear between the hardened metal surfaces of plungers and bushings used to create the high injector pressures. Insufficient lubricity in a fuel can lead to high maintenance costs associated with replacement of injector parts. ASTM standards D 5001, D 6078, and D 6079 describe methods used to characterize the effectiveness of lubricants in diesel.
- 6. Flash Point and Fuel Safety. Flash point temperatures are a measure of the propensity for a fuel to ignite when exposed to a flame or ignition source. Clothier et al[9] reports the approximate boiling ranges of gasoline and diesel to be 30-200°C and 160-330°C respectively. The lower ends of these ranges (i.e. the vapor pressures of hydrocarbons) tend to correlate with typical flash point temperatures of <-40°C for gasoline and >38°C (>56°C in some European countries) for diesel. Blending with low molecular weight hydrocarbons, alcohols, or ethers will tend to decrease flash point temperatures. ASTM standard D 92 provides the flash point measurement technique.

Due to safety and fugitive emissions considerations, it is desirable to use fuels with higher flash point temperatures to minimize the total content of fuel in the vapor phase; however, it is also important to avoid mixtures that form explosive mixtures as ambient temperatures. This latter precaution suggests that in some instances it may be safer to use fuels with higher vapor pressures if the vapor pressures displace oxygen in the fuel tank and lead to vapor phase mixtures that are richer than the explosive regime in the gas tank. Gasoline is widely used as a vehicular fuel despite its low flash point—some relate the safety and acceptance of this high vapor pressure fuel to the fact that it is so volatile that the fuel displaces oxygen



from the fuel storage devise and explosive mixtures are thus avoided.

CI engines have been manufactured and used with fuels having high vapor pressures such as neat ethaonol[10], and so, there is no inherent reason why fuels with flash points similar to gasoline cannot be used in diesel engines.. Typically,. While it is desirable for a CI fuel to have a high flash point temperature, fuel development will not be limited to blends with high flash point temperatures. A good blend stock balances pour point depression capabilities with increases in flash point temperatures.

The flash point of a Fischer-Tropsch formulation is a degree of freedom in designing that fuel. High flash points can be achieved by restricting the amount of more volatile components in the FTL and using additives with high flash point temperatures. Fuels that lead to rich airtuel mixtures in storage devices can be achieved by mixing with ethanol (having a very high activity and vapor pressure near that of pure ethanol), by keeping light components in FTL, and by mixing with greater quantities of volatile components.

7. Phase Behavior. One of the greatest development challenges toward the utilization of mixtures of ethanol with hydrocarbon fuels, including FTL, is the propensity for ethanol to partition in an aqueous-rich phase when the mixture of hydrocarbon and ethanol contacts water. As little as 0.25% water can lead to 90% of the ethanol in the hydrocarbon to form a hydrophilic phase containing the trace amount of water. When this phase separates and the bulk of this phase reaches the CI engine, the engine will stall. If this problem is overcome, the benefits of ethanol toward reducing engine emissions can be realized.

Prior to the engine testing reported in this paper, cloud point temperatures, pour point temperatures, cetane numbers, and phase behaviors of several representative formulations were evaluated and reported[11]. These preliminary laboratory analyses are summarized in Table 1.

Figure 2 shows the GC-MS analysis of the FTL product evaluated in preliminary studies[11, 12]. Compositions of FTL typically include C_5 to C_{24} hydrocarbons and are determined by process separation processes. The product of Figure 2 is liquid at room temperature and solidifies at 2°C (see Table 1)—a pour point temperature that is too high for much of the diesel-fuel market. A comparison of the FTL composition to FT CI fuel provides some insight into how the conventional 3-step fuel varies from the proposed 2-step fuel.

Figure 3 provides the GC-MS analysis of one of Syntroleum's FT CI fuels. The combination of no C₁₅₊ hydrocarbons and the chemical diversity introduced by the multitude of isomers leads to a substantial freezing point depression. The FT CI fuel has a cloud point of about – 54°C (see Table 1)—a typical value for advanced FT CI fuels. The primary benefit of the FT CI fuel (Figure 3) as compared to a FTL (Figure 2) is the reduced pour point temperature of FT CI fuel. The pour point of FTL can vary

based on process conditions. Table 1 summarizes the pour point data and other properties related to CI fuel performance. The viscosity and cetane number of FTL can be better than the FT CI fuel.

At a pour point of 2°C, the pour point temperature of the FTL is sufficiently low for much of the world for the entire year—a great starting point. For the remaining global market, a pour point temperature of 2°C is sufficient for much of the year. Furthermore, when the pour point temperature of the FTL is too high, both blend stocks (gasoline, hexanes, diethyl ether, ethanol ... etc) and additives (pour point depressants) can be used to improve the flow properties. As detailed by data of Table 1, blend stocks and additives can substantially improve pour/cloud points.

Based on preliminary data, low temperature operability (characterized by cloud, pour, or cold-flow temperature depending upon application) of FTL is the primary property that is at times insufficient; however, these properties can be controlled with blend stocks and additives. In addition, the composition of the FTL can be controlled by separation processes (typically vapor-liquid flash separations) to improve these properties.

In regard to using FTL as a vehicular fuel, the degrees of freedom are numerous, available data is extremely limited, and the opportunity to reduce production costs is great

EXPERIMENTAL PROCEDURE

These fuel development and engines tests were performed to (1) determine if FTL could be used as diesel fuels, (2) determine the performance of FTL in a typical diesel engine, and (3) evaluate the performance of mixtures formulated to reduce pour points and emissions.

Engine tests were performed on a Detroit Diesel 453T engine connected to a Pacemaker OX-365 dynamometer. This is a 2-stroke engine equipped with a supercharger. Engine emissions were analyzed with a J.U.M. Engineering Total Hydrocarbon Analyzer Model VE7, a Thermo Environmental Instruments Inc (Model 10 and Model 800) Chemiluminescent NO-NO₂-NO_x Analyzer, Beckman Industrial Model 850 Infrared Analyzers for CO and CO₂, and one Beckman Model 865 Infrared Industries Inc. Oxygen Analyzer.

Particulate samples were collected and weighed using 47mm, 1.0 micron, laminated TEFLON filters produced by Micron Separations Inc. CFR 40-86.139-90 weighing procedures were followed with modified CFR 40-86.110-94 sample collection procedures. Filter samples were weighed with a Denver Instruments Model D200DS balance. The modified experimental procedures did not use a dilution tunnel—straight exhaust was used.

With the exception of particulate analysis, emissions were monitored continuously with the calibration being checked at the beginning and end of each day of testing. The last thirty measurements at the indicated load were

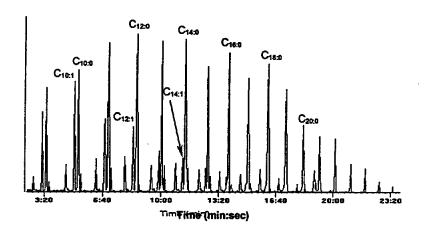


Figure 2. GC-MS of a Syntroleum FTL. Processed for low C6, C7 and C6 content.

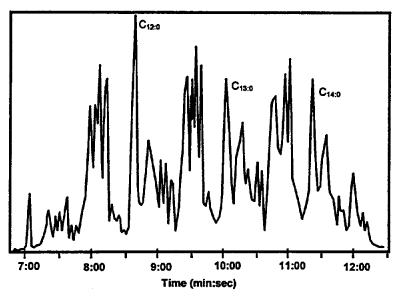


Figure 3. GC-MS of a Syntroleum FT CI fuel.

Table 1. Pour point temperatures, viscosities, and cetane numbers of select blends. The kinematic viscosities were measured at 40 °C. UI8094 is an additive designed to suppress the pour point temperature.

Base Fuel	Blend Stock	Blend Stock (mass%)	Cetane Number	Viscosity (mm²/s)	Pour Point (C)
37 CN Diesel	-	-	37	3.05	-13
FT CI fuel Distillate	-	-	>64	1.92	-54
C ₉ -C ₂₂ FTL	none	-	>67	2.2	2
и	Gasoline	30%	63	1.28	-6
. *	" + 240 ppm UI8094	*			-12 -
*	" + 850 ppm UI8094				-21
ĸ	Hexanes	30%			-12
#	Diethyl Ether	30%			-10
4	Ethanol	30%	33	1.78	3
•	Ethanol	20%	45	2.06	2
et.	ss.	10%	58	2.21	3

Table 2. Summary of test sequences used to test FTL and FTL formulation fuels.

Test Sequence 3

(Modified Off-Highway Test Cycle):

- a. US:2D diesel
- b. US 2D diesel
- c. US 1D diesel
- d. FTL-2 + 25% Gasoline
- e. FTL-2
- f. FTL-2 + 20% Ethanol
- g. FTL-2 + 16.5% Ethanol + 16.5% Diethyl Ether
- h. FTL-2 + 10% Ethanol + 10% Diethyl Ether
- i. FTL-2 + 25% Ethanol
- j. FTL-2
- k. US 1D diesel

Test Sequence 2

(40% Load):

- a. US 2D diesel
- FTL-1
- m. FTL-1 + 25% Gasoline
- a. US 2D diesel
- n. FTL-1 + 12.5% Ethanol + 12.5% Diethyl Ether

(80% Load):

- a. US 2D diesel
- a. US 2D diesel
- L FTL-1
- o. FTL-1 + 25% Hexanes
- n. FTL-1+ 12.5% Ethanol + 12.5% Diethyl Ether

Test Sequence 1

(40% Load):

- a. US 2D diesel
- I. FTL-1
- o. FTL-1 + 25% Hexanes
- m. FTL-1 + 25% Gasoline
- n. FTL-1 + 12.5% Ethanol + 12.5% Diethyl Ether
- a. US 2D diesel

averaged to obtain values for reporting. Analyses included carbon monoxide (except during test 3), carbon dioxide, oxygen, NO, NO $_{x}$, and hydrocarbons. A cold trap and filters were used prior to all analyses except the hydrocarbon analysis for which the sample lines were kept above 190°C. NO was found to represent >90% of NO $_{x}$ based on measurements during test 3.

Three similarly processed samples of FTL were used for the data of this paper: 1) the FTL used for preliminary data (Table 1), 2) FTL Sample 1 (FTL-1) and 3) FTL Sample 2 (FTL-2). Engine tests were conducted during three separate days (test sequences) using FTL-1 and FTL-2 as summarized in Table 2. The composition of the FTL used to generate Table 1 is described by Figure 2. The performance of US 1D was used to normalize efficiency and particulate matter data.



During test sequence 1 preliminary tests were conducted to confirm that the test fuels were capable of powering the engine and to generate protocol for switching fuels.

For test series 1, the load was kept constant at 40% and 1500 rpm with 1.5 liters of each fuel consumed. FTL-1 was used for these tests.

During test sequence 2 both 40% load and 80% load tests were performed with full emission's analyses and with particulate sampling. Emission's analysis procedures were developed to approximate those described in the Code of Federal Regulations (CFR). For these tests, fuels were switched at a constant load of 40% and 1500 rpm with 1.0 liters of each fuel consumed. The engine was then loaded to 80% and 1500 rpm with 2 liters of each fuel consumed. FTL-1 was used for these tests.

During test sequence 3 (5/5/98), a 3-mode test sequence was developed based on the 8-mode cycle of CFR 40-86.446-79. The 3-mode test sequence included about 5 minutes of operation at 80%, 50%, and 0% load. Each test sequence was completed prior to changing fuels with approximately 6 liters of fuel being consumed per test sequence. FTL-2 was used for these tests.

Although the chemical composition of the two FTL samples were not evaluated, pour point, cloud point, and cetane number data were determined by methods similar to those use for the data of Table 1[11].

RESULTS

Properties of Test Fuels — Cetane numbers were estimated using a constant volume combustor by methods similar to those used by Suppes et aland by Allard et al[11, 13, 14]. These data are summarized in Table 3. The trends are as expected with the possible exception of 25% gasoline in FTL which is higher than a similar mixture with hexanes—a value lower than 60 was anticipated. The FTL-2 formulations had cetane numbers that were consistently 1 to 3 higher than the FTL-1 formulations.

Pour point and cloud point data are summarized in Tables A1 and 4. The impact of UI 8092 and Cold Flow pour point depressants (supplied by Mid-Continental Chemical Corporation, Leawood, Kansas) were evaluated to determine their effectiveness in lowering pour points. FTL-2 has both a higher cloud point and a lower pour point than FTL summarized in Table 1. Slight variations in compositions can account for these difference properties.

Pour point additives were effective in lowering the pour point temperatures. Table A1 shows the impact of blend stock and additives on pour points and cloud points summarizing changes in cloud points and pour points. The lower two sets show decreases in cloud and pour points as a result of blend stocks and additives—only reductions <1.5°C were reported.

Table 3. Cetane numbers of FTL formulations and neat base fuels.

Fuel	Additive (@ 25%)	Cetane Number
c.		50
i.	Ethanol	51
Standard		58
0.	Hexanes	61
n.	Ethanol + DEE	61
d.	Gasoline	62
Standard		70
i.		71
i.		71
e.		>72

Table 4. Pour point and cloud point temperatures of FTL Sample 1 formulations. Data are in °C.

Hexane Conc. (mass %)	Cloud Point (C)	Pour Point (C)
0%	9.2	1
10%	7.5	-2.5
20%	5.7	-9.7
30%	4.7	-10.2

Engine Performance - The FTL powered the Detroit Diesel 453T engine without difficulty and without changes in performance. The one exception to this observation is that the engine received insufficient fuel and stopped running when insufficient back-pressure was maintained on the fuel line that feeds the injector The higher vapor pressure of the FTL (especially mixtures with diethyl ether) leads to cavitation if the pressure is too low on the fuel line—this problem was corrected with a valve and pressure gauge at the exit of the fuel line that circulates fuel through the injectors. In practice, Detroit Diesel uses a restrictive fitting at the recirculation line discharge in the cylinder head. The restrictive fitting comes in various sizes—a fitting designed for diesel may be inadequate if a fuel with both lower viscosity and higher vapor pressure is used instead of diesel. Back-pressure valves are available that would function at a broad range of fuel properties. A back-pressure of 20 psig was sufficient.

To determine maximum power output and maximum torque, the rack was placed at its maximum setting and torque was increased until engine failure occurred. The maximum power output and maximum torque characterize this performance and are summarized in Table 5.

Thermal Efficiency – Thermal efficiency is defined as the net work performed per fuel energy consumed. Fuel

Table 5. Maximum torque and power versus test fuels.

Operating Conditions

Fuel	ft-lbf	грm	hp	max ft-lbf	rpm
a.	429	2100	172	440	1890
b.	379	1410	102		
C.	398	2100	159		
d.	370	2100	148	380	1800
e.	365	2100	146	380	1800
f.	348	2100	139	360	1800
g.	340	2100	136	342	1800
h.	355	2100	142	360	1800
i.	337	2100	135	350	1800
j.	366	2100	146	375	1800
k.	402	2100	161	406	1800

Power of Engine at Maximum Torque

	Torqu ft-lbf	Speed rpm	Power hp	LHV X den (kJ/cc)	Power % US 1D
a./b.	429	2100	171.5		
C.	398	2100	159.1	0.0	99.5%
d.	370	2100	147.9	0.0	92.5%
e.	365	2100	145.9	0.0	91.3%
f.	348	2100	139.1	0.0	87.0%
g.	340	2100	135.9	0.0	85.0%
h.	355	2100	141.9	0.0	88.8%
i.	337	2100	134.7	0.0	84.3%
j.	366	2100	146.3	0.0	91.5%
k.	402	2100	160.7	0.0	100.5%

consumption increased slightly as the energy density of the fuel decreased; however, when the energy density was taken into account the thermal efficiencies were within the error of the method used to follow fuel consumption (except for ether mixtures which appeared to have evaporation losses). Errors were greater than anticipated due to the fuel return loop that often introduced vapor/bubbles into the graduated cylinder used to follow the volume of fuel consumed.

As a backup method to follow fuel consumption, a carbon balance was used (i.e., With engine speed is held constant, the carbon content of the exhaust was used to estimate the quantity of fuel consumed relative to a diesel reference fuel.). Table 6 provides heating values used to determine the fuel's lower heating value per carbon in the fuel. Using the values of Table 6, the carbon in the exhaust (carbon dioxide, carbon monoxide, and hydrocarbons) was directly related to the fuel consumption. The 20% ethanol and the two ethanolether mixtures exhibited a 2-3% increase in thermal efficiency based on this method. These calculations complement the positive deviations of these fuels illustrated by Figure 4. For the ether mixtures, these positive deviations could be due to evaporation of ether from the mixture; however, the positive deviation of the 20% ethanol mixture is believed to be real although minor at a 2-3% increase.

Table 6. Lower heating values (LHV) used to estimate the energy content per carbon in fuel.

	LHV (Btu/lb)	density (g/cc)	Density (kJ/cc)
Diesel	18500	0.86	37.0
FTL	18600	0.783	33.8
Ethanol	11500	0.794	21.2
Diethyl Ether	14571	0.714	24.2
	mass C mass fuel mass %	Formula	(Btu/C)
Diesel	86.5%	CH _{1,88}	21398
FTL	85.1%	CH _{2.1}	21855
Ethanol	52.2%	\circ	22042
	52.276	C₂H ₆ O	22042
Diethyl Ether	64.9%	(C ₂ H ₅) ₂ O	22042 22464

Table 7. Summary of emissions from first two tests at 40% and 80% loads and 1500 rpm.

	%	‱ %	(ppm)	(ppm)	(ppm)	C	PM
Test Sequent	ce 2						
	NI/A	C 00/	4-	045	4= 4		
a.	N/A	6.0%	47	615	17.1	280	
i.	N/A	5.8%	77	555	17.1	282	100%
m.	N/A	5.8%	115	557	17.0	282	90%
a.	N/A	6.1%	50	628	17.0	N/A	100%
n.	N/A	5.6%	116	577	17.3	287	70%
80% Load							
a.	0.12%	8.4%	72	750	14.5	284	93%
a.	0.11%	7.8%	56	768	15.0	289	107%
l.	0.11%	7.2%	98	647	15.4	289	81%
0.	0.10%	6.8%	133	621	15.6	288	68%
n.	0.09%	7.5%	132	655	14.9	287	55%
Test Sequence	æ 1						
40% Load							
a.	0.01%	6.0%	55	584	16.8		
I.	0.01%	5.7%	85	516	16.9		
o.	0.01%	5.7%	131	520	16.8		
m.	0.01%	5.6%	135	526	16.9		
n.	0.01%	5.8%	61	539	16.9		
a.	0.01%	5.9%	61	583	16.9		

Emissions – Table A2 summarizes the emissions for FTL-2 formulations tested during the third and most exhaustive set of tests. This same data is presented by Figures 5 and 6. Table 7 summarizes the emissions for the FTL-1 formulations tested in April of 1998. Figure 7 and Table 8 summarize the particulate matter emissions for the FTL-2 runs. In addition to these gravimetric analyses, Figures 8 and 9 present photos of the actual filter paper samples exposed to the same flow rate at a fixed time.

Table 8. Summary of impact of fuel on particulate emissions for FTL-2 runs. Data is reported in percent of particulate matter collected in two minutes of sample at a constant flow rate. The percent is relative to US1D performance for which 0.44 mg were collected at 50% load and 1.66 mg were collected at 80% load.

Fuel	Blendstock	50% Load	80% Load
a.		151%	88%
C.		100%	100%
d.	Gasoline	120%	77%
e.		95%	82%
f.	Ethanol Ethanol +	60%	51%
g.	Diethyl Ether Ethanol +	72%	31%
h.	Diethyl Ether	70%	49%
i.	Ethanol	51%	37%

DISCUSSION

The performance of diesel, FTL, and FTL mixtures with gasoline, hexanes, ethanol, and an equal mass mixture of ethanol and diethyl ether were evaluated in the laboratory and in a heavy duty, two-stroke diesel engine. To provide reliable operation, a needle valve was installed at the fuel discharge line returning from the injector. This valve was used to increase the static pressure of the fuel and prevent cavitation. Restrictive orifices are typically put on engine blocks to meet this need.

Laboratory Analyses – Cetane numbers for the FTL samples were greater than 70. Of the fuels tested, the US 1D fuel had the lowest cetane number. Ethanol had the greatest impact on the cetane number of the FTL with a cetane number of 51 in a 25% ethanol solution. The cetane numbers of the other mixtures were between 60 and 70—well above national diesel standards.

The cloud point temperatures of FTL-2 were fairly high at about 9°C while pour points were low at -19°C. Hydrocarbon blend stocks and ether were the most effective in reducing cloud points. In an atypical manner, 1000 ppm treatments of the pour point depressants had more than twice the impact of 500 ppm treatments—this phenomena should be investigated further.

Hydrocarbon and ether blend stocks were able to lower cloud points by 4°C and pour points by 6°C with hydrocarbon application at 20 mass% (Table A1). These trends follow what is predicted by freezing point depression theory.

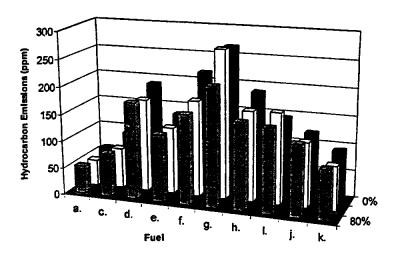


Figure 5. Hydrocarbon emissions in order fuels were tested at 80%, 50%, and 0% load.

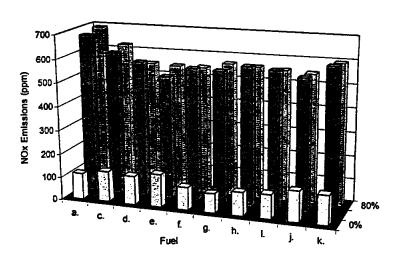


Figure 6. NOx emissions in order fuels were tested at 0%, 50%, and 80% load.

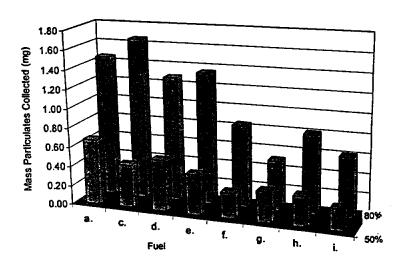
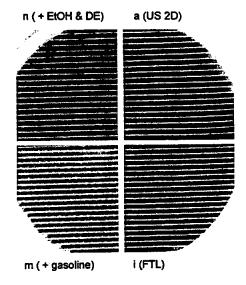


Figure 7. Summary of particle emissions at 80% load (back) and 50% load (front).

40% Load



80% Load

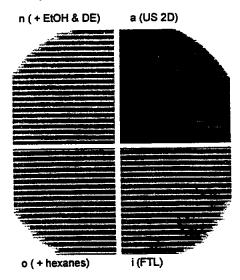
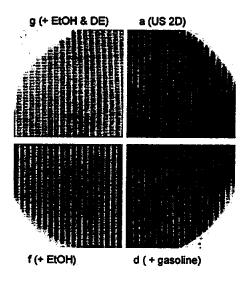


Figure 8. Filter samples illustrating lighter color of soot in formulations containing oxygenates for FTL-1 engine tests.

While ethanol was not effective in lowering cloud or pour points, it is believed that ethanol will be effective in lowering the more important low temperature flow properties (ASTM Standard D-4539) since ethanol lowers the viscosity of the fuel. For those samples with cloud points above 5°C, flow was unhindered until temperatures of about 2°C were reached.

Pour point depressants were able to add an additional 8 degrees to the reductions in pour points. Pour points as low as -30°C were achieved. Consistent with freezing point depression theory, the pour point additive did not impact the onset of solids formation as observed in the cloud point. It is reasonable to assume that pour point depressants did not impact the fraction of solids formed at a given temperature; rather, the additive impacted the morphology of the crystals.

50% Load



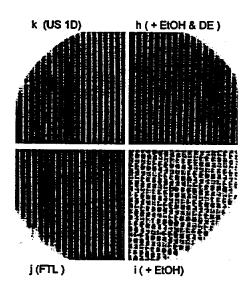


Figure 9. Filter samples illustrating lighter color of soot in formulations containing oxygenates for FTL-2 engine tests.

Performance – The energy density of the fuel had a direct bearing on both the maximum power output and torque. As illustrated by Figure 10, to a first approximation the maximum power output is directly proportional to lower heating value reported in energy per volume (energy density, kJ/cc)—the engine power is limited by the volume of fuel that can be injected by the fuel injectors. This can be easily corrected in most modern engine designs by tuning the injectors to icrease the maximum amount of fuel that can be ijected. The formulations containing diethyl ether exhibited the largest positive deviations from this correlation since they had the lowest energy density.

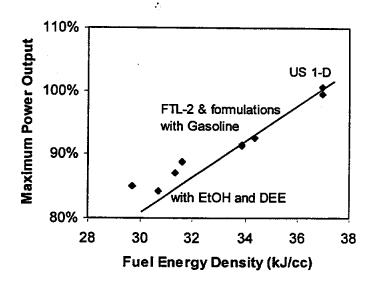


Figure 10. Impact of fuel energy density on maximum power output of engine.

The line of Figure 10 is for the power output directly proportional to the energy density of the fuel. The positive deviations of diethyl ether from this correlation is in part due to the volatility of diethyl ether—after the fuel is circulated through the injectors it returns to the feed tank and the more volatile components can evaporate due to the heat absorbed from the injectors. Normally, the increased temperature of the diesel would not impact observations; however, due to the high volatility of diethyl ether, part of the diethyl ether evaporates (and is lost), thereby lowering the content of diethyl ether and indirectly increasing the heating value of the fuel (now more concentrated in FTL).

No adverse impacts on the thermal efficiency were detected as a result of the fuels. In fact, mixtures containing ≤20% ethanol appeared to have a 2-3% increase in efficiency. Such increases in thermal efficiency have been observed with ethanol by other researchers where the thermal efficiency would typically peak at ethanol concentrations between 5 and 20%. Further research is needed to evaluate the extent to which thermal efficiency is increased.

Emissions - The FTL and all mixtures increased hydrocarbon emissions. The mixture containing 33% of an equal mass mixture of ethanol and diethyl ether exhibited the greatest hydrocarbon emissions at a 3.5 fold increase over US 1D fuel. US 1D is used for comparison because most fleet managers recognize the US 1D is preferred for applications that are particularly sensitive to emissions. The FTL exhibited a 50% increase in hydrocarbon emissions over US 1D fuel, and ethanol exhibited a 100% increase in hydrocarbon emissions. To a first approximation, the hydrocarbon emissions correlate with the volatility of the fuel. A possible mechanism for the increased hydrocarbon emissions includes the rapid evaporation of the fuel after being sprayed into the engine followed by convection to regions of the cylinder where the stoichiometry is too

lean to lead to good combustion. Even at a 100% increase over the diesel baseline, the hydrocarbon emissions are below those typical of spark-ignition engines. In addition, the hydrocarbon emissions can be readily decreased via catalytic converters and may even be desired to facilitate the reduction of NO_x emissions.

Table 9 presents the NO_x and hydrocarbon emissions data for FTL-2 formulations as reported in the preferred form of grams of emissions per brake horsepower hour (bhp-hr). The NO_x and hydrocarbon emissions are relatively high compared to today's highway engines as might be expected for a 2-stroke, 1993 off-highway engine. The 1998-2004 hydrocarbon and NO_x emissions are 1.3 and 4.0 g/bhp-hr respectively. It is likely that the FTL and FTL mixtures would be within current highway engine specifications when running in a cleaner-burning engine. The ratio of hydrocarbon to NO_x

emissions for the FTL and FTL with ethanol fuels are very close to the ratio of the specifications.

Performance advantages of the FTL and its mixtures included reduced NO_x and particulate emissions. Each of the formulations containing FTL produced about 10% reduction in NO_x emissions. Particulate emission varied as follows:

- Slight reduction FTL and FTL with 25% gasoline.
- 30% reduction FTL with 25% hexanes
- 30-50% reduction mixtures containing 20% or greater oxygenate (including ethanol) at 50% load.
- 50-70% reduction mixtures containing 20% or greater oxygenate (including ethanol) at 80% load.

Table 9. HC and NOx emissions on gram per bhp-hr basis.

Fuel	Speed (rpm)	Torque (ft-lb)	Work (bhp)	Air Flow (kg/hr)		NO _x np-hr) Load)		NO _x np-hr) Load)
a.	1465	313	87	785	0.5	6.2		
a.	1507	202	58	712			0.6	8.3
C.	1454	308	85	775	0.7	5.7		
C.	1502	200	57	708			0.9	7.5
d.	1468	302	84	77 7	1.6	5.0		
d.	1500	199	57	706			2.1	7.2
e.	1440	307	84	766	1.1	5.0		
e.	1448	301	83	766	1.1	5.0		
e.	1485	199	56	699			1.5	6.5
f.	1469	303	85	779	1.5	5.0		
f,	1520	195	56	712			2.2	7.1
g.	1497	301	86	792	2.0	5.2		
g.	1529	195	57	716			3.4	7.0
h.	1465	301	84	775	1.5	5.2		
h.	1513	199	57	712			2.1	7.3
i.	1467	307	86	781	1.4	5.0		
i.	1516	196	57	711			2.1	7.2
j.	1485	303	86	787	1.2	5.0		
j.	1530	197	57	718			.1.5	6.9
j.	1528	195	57	715			1.5	7.4
k.	1479	310	87	790	8.0	5.4		
k.	1510	196	56	708			1.0	7.6

To supplement data on the mass of particulate matter in the exhaust, the opacity of the filters used to collect the samples were recorded. The photos illustrate that in addition to producing less particulate matter, the FTL blends also produce a lighter colored soot. In the case of fuels containing ethanol and/or diethyl ether, the soot is markedly lighter in color. This lighter color provides better aesthetics and indicates that the particles have a higher hydrogen content (lower carbon content). This higher hydrogen content may be a result of a relatively large fraction of the solids originating from the condensation of hydrocarbons in the gas phase and may present opportunities to further reduce the mass of particulate matter with high temperature oxidation of the hydrocarbons over a catalytic converter. Changes in particle size may also have influenced to color of the particulate matter.

The combination of reduced NOx and reduced particulate emissions is widely pursued in CI engine technology to meet anticipated EPA regulations.

CONCLUSIONS

Diesel engine tests were performed with diesel and neat Fisher-Tropsch liquids FTL as well as FTL formulations containing (1) 25% gasoline; (2) 25% hexanes; (3) 20%, 25%, and 33% of a equal volume mixture of ethanol and diethyl ether; and (4) 20% and 25% ethanol. A three-mode test sequence was performed consistent with heavy duty diesel engine applications and each of the fuels met or exceeded goals on reduced emissions and pperability of the unmodified engine.

Two disadvantages of the FTL formulations were lower peak power capabilities due to the reduced energy densities of the fuels and increased hydrocarbon emissions. Power output can be easily corrected by using properly sized injectors which should add no additional cost. Hydrocarbon emissions were below typical values for spark-ignition engines and could be reduced with a catalytic converter. Higher hydrocarbon emissions could also be a potential advantage if catalysts are developed that allow the hydrocarbons to be destroyed while reducing NO_x emissions.

Preferred formulations reduced NO_x emissions by 10% and particulate emissions by >50%. Furthermore, the particulate emissions were not as dark as diesel soot. These significant performance advantages could provide a tremendous market potential.

ACKNOWLEDGEMENTS

The Fischer-Tropsch liquids used for these studies and funding for this project were provided by the Syntroleum Corporation, their support is greatly appreciated. No hydrocracked products were tested. Jim Elder of the

MidContinental Chemical Company in DeSoto, KS, provided the pour-point depressants.

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Table A1. Pour points and cloud points of FTL-2. Data are Temperature in degrees C.

									1 (
		Cloud Points		Pou	Pour Points			Cloud Points			Pour Points			
		UI 8092 Add. (ppm)			UI 8092 Add. (ppm)		Cold Flow Add. (ppm)			Cold Flow Add. (ppm)				
	1	01 603.		1000			000			000	0		000	
	00/1	11.0	10.5	10.3			22.8	11.0	7.7	5.8	-19.0	-17.5 -	22.7	
	0%			11.2			24.3	12.0	8.9	6.3	1		24.7	
Ethanol	10%	12.0	10.8				23.9	13.0	10.4	6.8			25.3	
	20%	13.0	10.9	12.3				11.0	6.0	5.4			26.3	
Hexanes	10%	-11.0	9.0	9.1		_	26.6	18	5.1	4.6	-23.0		29.7	
	20%	7.0	6.3	5.9			31.2	7.0			-19.0	_	24.7	
DEE	10%	10.0	10.1	9.8			27.3	10.0	7.1	6.0	•		28.8	
	20%	8.5	8.5	8.4		-	30.8	8.5	6.7	6.3	-23.0			
Gasoline	10%	9.5	9.2	9.1			26.2	9.5	7.7	5.5	-20.0		25.8	
	20%	7.5	6.3	5.9			30.6	7.5	5.1	4.6			29.3	
#1 Diesel	10%	10.5	9.7	9.4	-19.0	-20.8 -	21.7	10.5	7.7	5.3			25.0	
	20%	8.0	8.5	8.4	-21.0	-22.2 -	24.0	8.0	7.4	4.8			26.3	
EtOH/DEE	10%		10,5	10.3	-20.0	-21.2 -	27.8	12.5	8.9	6.3	1		-24.7	
Lto, "DEL	20%		10.6	10.7	-22.0	-23.2 -	-29.7	12.5	9.2	6.8	-22.0	-21.5 -	.29.7	
	2070	12.0						<u></u>						
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		0	500	1000		500	1000		000 .					
		1					1						-2	
Ethanol	10%												-3	
	20%				1	_			_			-6	-4	
Hexanes	10%	•			ı	-3	-4		-2		1 .		-7	
	20%	-4	-4	-4	-4	-7	-8	4	-3		-4	-7		
DEE	10%			1	-		-5					-4	-2	
	20%		-2	-2	-4	-7	-8	-3		l l	-4	-7	-6	
Gasoline	10%			ı		-3	-3			1		-3	-3	
Casomio	20%	9	-4	-4		-6	-8	-4	-3			-6	-7	
#1 Discol	10%			•	i		•			- 1			-2	
#1 Diesel	20%	E .	-2	-2	-2	-3		-3			-2		-4	
T.O. UDSS			-2	-2	-	-2	-5						-2	
EtOH/DEE	10%			1	-3	-4	-7				-3	-4	-7	
	20%	`			-3			<u> </u>			L			
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			oud Poin			Pour Points			Cloud Points Cold Flow Add. (ppm)			Cold Flow Add. (ppm)		
		UI 809	92 Add.			2 Add. (0 500 1000			
		0	500	1000	0	500	1000	0		1000		300	1000	
						. –	-4		-3	-5				
Ethanol	10%	6		1			-5	1	-3	-6	1		-6	
	20%	6	-2				-5		-3	-6			-6	
Hexanes	10%		-2	-2		-2	-7		<i>-</i> 5	-6		-3	-6	
	20%			ļ		-3	-8	l l	-2	-2			-7	
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Gasoline	109			- 1	1	-2	-6		-2	-4	1		-6	
Gasoine	209			-2	1	-5	-11		-2	-3		-4	-9	
## Pt 1				-41		-5 -2	-3		-3	-5			- 6	
#1 Diesel	109			- 1		-2	-3		-	-3			-5	
	209		_	ا			-8		-4	-6			-5	
EtOH/DEE	109		-2	-2			-8		-3	-6			-8	
	209	%	-2	-2	1		-01		-5					

Table A2. Summary of gas phase analysis of engine exhaust for FTL-2 formulations.

Fuel	Target Speed	Load %	CO2 %	HC (ppm)	NO (ppm)	O2 %	Speed (rpm)	Torque (ft-fb)	T (C)	Speed (rpm)	Torque (ft-lb)
Start Calibration, zero gas	(rpm)		0.1	0	0	0.0	-5	-1	21.2	-5	-1
Start Calibration, span gas			30.1	902	897	21.0			21		
End Calibration, zero gas			0.3	4	0	0.1	-4	-1		-4	-1
End Calibration, span gas			30.1	882	876	20.0					
a.	rated	100%	10.0	87	872	12.8	2140	389	287	2140	389
a.	rated	100%	10.0	79	928	12.9	2076	397	288	2076	397
a.	rated	75%	8.6	69	757	14.6	2305	291	289	2305	291
a.	rated	50%	7.0	61	617	16.4	2320	190	289	2320	190
a.	rated	10%	3.4	66	198	20.6	2385	41	223	2385	41
b.	1500	80%	7.3	51	692	16.0	1465	313	289	1465	313
b.	1500	50%	6.4	48	677	17.2	1507	202	289	1507	202
b .	1500	0%	1.5	57	113	22.9	1613	9	155	1613	9
C.	1500	80%	7.3	79	622	16.1	1454	308	289	1454	308
C.	1500	50%	6.2	75	609	17.4	1502	200	289	1502	200
c.	1500	0%	2.0	92	133	22.3	1618	8	154	1618	8
d.	1500	80%	6.9	178	548	16.3	1468	302	289	1468	302
d.	1500	50%	6.0	171	576	17.5	1500	199	290	1500	199
d.	1500	0%	1.8	189	125	22.4	1639	8	162	1639	8
e.	1500	80%	6.9	122	550	16.2	1440	307	290	1440	307
e.	1500	50%	6.6	124	544	16.5	1448	301	290	1448	301
e.	1500	50%	5.9	124	523	17.5	1485	199	290	1485	199
e	1500	0%	1.9	136	144	22.4	1600	8	161	1600	8
f.	1500	80%	6.4	164	545	16.6	1469	303	290	1469	303
f.	1500	50%	5.5	177	564	17.8	1520	195	290	1520	195
f	1500	0%	1.6	217	99	22.5	1619	8	151	1619	8
g.	1500	80%	6.3	218	567	16.9	1497	301	290	1497	301
g.	1500	50%	5.5	272	559	17.9	1529	195	289	1529	195
g .	1500	0%	1.7	267	84	22.4	1650	7	153	1650	7
h.	1500	80%	6.3	159	560	16.9	1465	301	286	1465	301
h.	1500	50%	5.5	166	586	17.9	1513	199	264	1513	199
<u>h.</u>	1500	0%	1.7	187	102	22.4	1101	7	140	1101	7
i.	1500	80%	6.6	154	553	16.6	1467	307	289	1467	307
i.	1500	50%	5.6	168	576	18.0	1516	196	290	1516	196
<u>i.</u>	1500	0%	1.8	145	106	22.8	569	5	131	569	5
į.	1500	80%	6.2	130	546	17.0	1485	303	290	1485	303
j.	1500	50%	5.5	119	555	18.0	1530	197	290	1530	197
i·	1500	50%	5.4	122	584	18.1	1528	195	290	1528	195
J.	1500	0%	1.9	122	133	22.4	1660	7	153	1660	7
k.	1500	80%	6.5	91	597	16.9	1479	310	290	1479	310
k.	1500	50%	5.6	82	608	18.1	1510	196	290	1510	196
<u>k.</u>	1500	0%	1.9	93	128	22.4	1637	8	150	1637	8